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MATHEMATICAL MODEL OF PHASE COMPOSITION DIAGRAM OF CaO - SiO_2 - Fe_2O_3 - B_2O_3 SYSTEM

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There is developed a method of the mathematical description of a phase composition diagram of n-component systems in the (n - 1) - dimensional space. There is built a phase composition diagram of the CaO - SiO_2 - Fe_2O_3 - B_2O_3 system and developed its mathematical model. It permits to determine its phase composition according to the chemical composition of the initial material. There is also solved the reverse problem: determination of the appearance and quantity of components of the initial furnace charge for obtaining a product of the required phase composition. An example of the use of models to estimate the phase composition of iron ore pellets.

Key words: Phase composition, diagram CaO - SiO_2 - Fe_2O_3 - B_2O_3 mathematical models, metallurgy, pellet

INTRODUCTION

The CaO - SiO_2 - Fe_2O_3 system is an important component of multicomponent systems, and for a number of productions has also an independent value. It is included, for example, into the six - component CaO - SiO_2 - Al_2O_3 – MgO – FeO - Fe_2O_3 system which describes the processes of production of cement clinker, ceramics, refractory materials, smelting of cast iron, steel, ferroalloys and other production. As independent it describes, for example, the processes of production of pellets by the annealing method from ferriferous quartzite. For this reason this system is a subject of continuous studies.

The CaO - SiO_2 - Fe_2O_3 system state diagram was repeatedly studied, specified and in the graphic view, according to Osborn and Muena, provided in the work by Berezhnoy [1]. There is also proposed the phase composition diagram of this system in the form of elementary triangles of the coexisting phases.

In this work there was defined the purpose of studying the regularities of phase forming when entering boric anhydride (B_2O_3) in the CaO - SiO_2 - Fe_2O_3 system.

It has a strong effect of lowering viscosity, refractoriness, surface tension of the silicate systems, to construct the phase composition diagram and to develop its mathematical model.

METHODS OF STUDYING

The method which is based on the thermodynamic assessment of the possibility of the secondary compounds coexistence, as well as the principles of topology of diagrams [1, 2] is applied for the development of the phase composition diagram.

In the graphic representation the CaO - SiO_2 - Fe_2O_3 - B_2O_3 system represents a tetra-hedron made of private systems (Table 1).

Table 1 **List and number of private systems**

Number of		Systems
components	systems	
1	4	CaO; SiO_2; Fe_2O_3; B_2O_3
2	6	CaO - SiO_2; CaO - Fe_2O_3; CaO - B_2O_3; SiO_2 - Fe_2O_3; SiO_2 - B_2O_3; Fe_2O_3 - B_2O_3;
3	4	CaO - SiO_2 - Fe_2O_3, CaO - SiO_2 - B_2O_3, CaO - Fe_2O_3 - B_2O_3, SiO_2 - Fe_2O_3 - B_2O_3
4	1	CaO - SiO_2 - Fe_2O_3 - B_2O_3.

The data of the carried out studies were planned to be used first of all for high-temperature processes. Therefore for the development of a diagram from the reference media there were selected stable (congruently melting) compounds. They were applied on the triangle of compositions. By triangulation in each three-component system there was determined the number of elementary triangles of the coexisting phases that gave the phase composition diagram. Based on the triangulation of ternary systems it was built diagram of the phase composition of the quaternary system CaO - SiO_2 - Fe_2O_3 - B_2O_3. (For brevity phase designated as CaO - C, SiO_2 - S, 2CaO · SiO_2 - C_2S etc).

RESULTS OF THE STUDIES AND THEIR DISCUSSION

CaO – SiO_2 – Fe_2O_3 system.

It is made of three binary systems: C - S, C - F and S - F [1]. In the first one there are formed four calcium

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silicates: C_3S, C_2S, CS and C_3S_2, the first and last of which melt with decomposition and therefore they are not accepted for the development of the diagram. In the second one (C - F) there are three ferrites of calcium: two-calcic C_2F one - calcic CF and semi - calcic CF_2. C_2F is stable. In the third binary system (S - F) there are no chemical compounds [1]. Triple compounds are absent in the system. Triangulation of C – S - F system executed with the use of methods [1, 2] finds in it 4 triangles of the coexisting phases (Figure 1): 1,C - C_2S - C_2F, 2,C_2S - C_2F - F, 3,C_2S – F - CS, 4,F – CS - S

$CaO – SiO_2 – B_2O_3$ system.

This system was considered in work [3]. From the list of presented there phases there are excluded C_2B_3 and CBS_2, which are formed only by the method of hydrothermal synthesis. By data [4] in this system there are two triple compounds: C_5BS and $C_{11}BS_4$. But they melt with decomposition and therefore they cannot be used for the development of the diagram.

The compounds which are available in the binary C - S system were listed above, in the S - B system chemical compounds are absent, and in the C - B system there was established the existence of four calcium borates: C_3B, C_2B, CB and CB_2, from which diborate (CB_2) melts with decomposition [5]. So, for the development of the diagram there were selected 5 binary phases (C_2S, CS, C_3B, C_2B, CB). Triangulation gives the diagram (Figure 1) in which we allocate 6 elementary triangles of the coexisting phases: 1,C - C_3B - C_2S, 2,C_3B - C_2B - C_2S, 3,C_2S - C_2B - CS, 4,C_2B – CB - CS, 5,CB – CS - S, 6, CB – S - B.

$CaO – Fe_2O_3 – B_2O_3$ system.

In literature there are no phase composition diagrams of the $CaO - Fe_2O_3 - B_2O_3$ system. Therefore triangulation is carried out by the data of its binary systems. C - F and C - B systems were considered above. In the $B_2O_3 - Fe_2O_3$ system according to data [6] there are two chemical compounds: FB и FB_3. In the quadrangle of the C_2B - C_3B - C_2F - F (Figure 1) substances there was written the reaction 2 C_2B + C_2F = 2 C_3B + F. Calculation using complex software HSC Chemistry 5.1 (Finland) shows that it $DG_{298,15\ K}$ = - 71,4, and $DG_{1\ 738K}$ = - 2,07 кJ/mole, giving the possibility to claim the coexistence of the reaction products (C_3B and F) in a broad range of temperatures, in which connection on the diagram they were connected with a straight line. The existence of this line geometrically reveals the only option of coexistence of two-calcic ferrite (C_2F) with three-calcic borate (C_3B).

In the known literature there were not found thermodynamic data for $Fe_2O_3 \cdot 3\ B_2O_3$ and $Fe_2O_3 \cdot B_2O_3$, therefore for the further triangulation there were attracted other principles. The preference of interaction of the strong base (CaO) with the strong acid oxide (B_2O_3) rather than the same base with feeble acid oxide (Fe_2O_3), permitted to consider the following reactions proceeding in the forward direction:

$$2\ (3\ CaO \cdot B_2O_3) + Fe_2O_3 \cdot B_2O_3 = = 3\ (2\ CaO \cdot B_2O_3) + Fe_2O_3 \qquad (1)$$

$$2\ CaO \cdot B_2O_3 + Fe_2O_3 \cdot B_2O_3 = 2\ (CaO \cdot B_2O_3) + Fe_2O_3 \qquad (2)$$

Based on this, the products of the given reactions (C_2B and F, as well as CB and F) on the triple diagram of the studied C – F - B system were connected by straight lines as the coexisting phases. As for the phase $Fe_2O_3 \cdot 3\ B_2O_3$, after the executed triangulation for it there is the only thing the option of coexistence with $CaO \cdot B_2O_3$. It should be noted that the executed splitting does not contradict the rule of coexistence of congruent compounds with congruent and isomorphic [1, 7]. Thus, in this system triangulation reveals 7 elementary triangles of coexisting phases: 1,C - C_3B - C_2F; 2,C_3B - C_2F - F; 3,C_3B – F - C_2B; 4, C_2B – F - CB; 5,CB – F - FB; 6, CB – FB - FB_3; 7, CB - FB_3 - B (Figure 1).

$SiO_2 – Fe_2O_3 – B_2O_3$ system.

The phase composition diagram of the S – F - B system is also constructed for the first time. In binary $SiO_2 - Fe_2O_3$ and $SiO_2 - B_2O_3$ systems chemical compounds are absent [1, 5], and in $Fe_2O_3 - B_2O_3$ system there are two already mentioned compounds FB and FB_3. Therefore it is broken into three elementary triangles of the coexisting phases 11,S – F - FB, 2,S – FB - FB_3 и 3,S - FB_3 - B (Figure 1).

$CaO – SiO_2 – Fe_2O_3 – B_2O_3$ system.

The existence of the phase composition diagrams of private three - component systems permitted to make splitting into elementary tetrahedrons the four-component $CaO - SiO_2 - Fe_2O_3 - B_2O_3$ system. In addition to the used above ones there was also used the method of “closing” triangles on the tetrahedron by comparison of their compositions [1, 7], which allowed to beat the $CaO - SiO_2 - Fe_2O_3 - B_2O_3$ system 9 elementary tetrahedrons of coexisting phases: 1,CB – B - FB_3-S, 2,CB - FB_3 – S - FB, 3,CB – S – FB – F, 4,CB – S – F – CS, 5,CB – CS – F - C_2B, 6,C_2B – CS – F - C_2S, 7,C_2S - C_2B - C_3B - F, 8,C_3B - C_2S – F - C_2F, 9,C_3B - C_2S - C_2F - C. In Figure there is shown the obtained tetrahedron and its scanning by the edges which can be used for determination of the phase composition.

But searching for the phase composition by geometrical creations in the tetrahedron is complicated, and in five -, six - and more component systems is impossible. The single way is the development of a mathematical model. In this paper, we proposed a method used mathematical description of phase diagrams of the composition, based on the balance of the distribution of the initial phases of the oxides in the image [8]. The mathematical model is created for each (seven) elementary tetrahedron. For example, to obtain such a tetrahedron №1 equation: CB=2,2523·C_0, B= - 1,2523 · C_0 - 1,3127 · F_0 + 1·B_0, FB_3 = 2,3127 · F_0, S = 1· S_0, wherein through

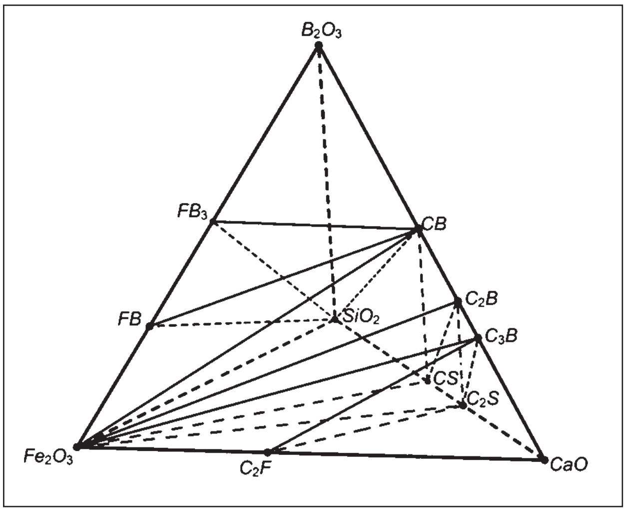

Figure 1 Phase composition diagrams of the CaO - SiO_2 - Fe_2O_3 - B_2O_3

C_0, F_0, B_0 and S_0 designated contents of CaO, Fe_2O_3, B_2O_3 and SiO_2 in the feed in weight percent based on chemical analysis.

In metallurgy importance attached to the formation of an optimal phase composition of agglomerated iron ore (sinter, pellet), giving it a high strength [9,10]. The above model was used as an example for these purposes. In Table 2 there is provided the chemical and phase composition of the sheaf (dead rock) of pellets from ferrous quartzite of the Northern Mining and Processing works (Ukraine) [11]. It is described by the private CaO - SiO_2 - Fe_2O_3 system considered above. The low - base ((CaO / SiO_2 = 0,3) and produced at the factory (CaO / SiO_2 = 0,65) pellets are placed in elementary triangle 4, F – CS - S. With growing the degree of fluxing (CaO additives) as a part of the sheaf, there increases the quantity of wollastonite (from 50 to 78 %) which recrystallizing in the reducing conditions of the blast furnace is the reason of the low durability of these pellets [11].

When increasing basicity to 1,2 and 1,5 the sheaf moves to the calcic corner of the diagram and gets to the field of elementary triangle C_2S - F - CS. Here alongside with wollastonite (CS) there is two - calcic silicate (C_2S) which though reduces crystallinity of the sheaf but is dangerous because of the possibility of inversion with changing the volume [12] that can lead to destruction of pellets. The additive of boric anhydride sharply reduces the field of crystallization of two-calcic silicate

Table 2 **Calculated phase composition of the mixed pellets made of ferrous quartzite concentrates**

$\frac{CaO}{SiO_2}$	Chemical and phase composition / %									
	CaO	SiO_2	Fe_2O_3	B_2O_3	C_2S	CS	F	S	C_2B	CB
0,3	24,2	52,8	23,0			50,1	23,0	26,9		
0,5	28,2	50,2	21,6			58,4	21,6	20,0		
1,0	37,5	42,5	20,0			77,6	20,0	2,4		
1,2	42,2	42,8	15,0		6,9	78,1	15,0			
1,5	46,5	39,5	14,0		29,6	56,4	14,0			
1,2	42,0	42,6	14,9	0,5	4,4	79,4	14,9		1,3	
1,2	41,8	42,4	14,9	1,0	1,8	80,7	14,9		2,6	
1,2	41,4	41,9	14,7	2,0		81,3	14,7		2,0	2,0

(C_2S) and already at 2% of B_2O_3 the sheaf leaves this dangerous field moving to tetrahedron 5, CB – CS – F - C_2B (Table 2).

It is the consequence of thermodynamic preference of borate formation rather than calcium silicates. All described is a cardinal measure of disposal from 2 $CaO \cdot SiO_2$. But if it is necessary for technological reasons in the pellets to maintain a high ratio $CaO \cdot SiO2$ and at the same time to prevent its destruction, you can do more economical measures.The matter is that in the presence of B_2O_3 the replacement of $(SiO_4)^4$ anion, two-calcic silicate by $(BO_4)^5$ anion, boric anhydride with formation of a solid solution stabilizes the high-temperature (not breaking up) forms $2CaO{\cdot}SiO_2$, and for this purpose there is sufficient only 0,25 – 0,50 % of B_2O_3[13].

The positive effect of B_2O_3 on the properties of iron-ore pellets shows us the laboratory and industrial trials [14].

It should be also noted that when processing these materials in the blast furnace, B_2O_3 contained in them will partially pass into slag reducing its refractoriness and viscosity, and partially will be reduced into cast iron and in to pass subsequently into steel and rolled metal, considerably improving their properties at concentrations making from 0,001 to 0,003 % [15].

CONCLUSION

There is built a diagram of the phase composition of the CaO – SiO_2 - Fe_2O_3 - B_2O_3 system and developed its mathematical model. It permits to determine its phase composition by the chemical composition of the material. Using the model it is also possible to define the type and quantity of components of the initial furnace charge for obtaining the product of the required phase composition. It is shown that the addition to the system CaO - SiO_2 - Fe_2O_3 boric anhydride reduces field dicalcium silicate crystallization and stabilizes the collapse of materials containing it. An example of the positive impact of B_2O_3 on the properties of iron – ore pellets.

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