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MATHEMATICAL MODELS OF VISCOSITY DIAGRAMS AND CRYSTALLIZATION TEMPERATURES OF MELTS OF THE $CaO – SiO_2 – Al_2O_3 – B_2O_3$ SYSTEM

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Mathematical diagrams of viscosity and crystallization temperatures of melts of the $CaO – SiO_2 – Al_2O_3 – B_2O_3$ system were created. To obtain them, experimental studies were carried out using the simplex-lattice method of experiment planning. It was used to study 35 slags containing (wt.%) 9.8-52 CaO, 33.6-70.4 SiO_2, 16.0-51.52 Al_2O_3, 0-20 B_2O_3. The experiments were carried out on an electrovibrational viscometer in molybdenum equipment, in a stream of purified argon in the temperature range of 1 473–1 923 K.

Keywords: $CaO – SiO_2 – Al_2O_3 – B_2O_3$, mathematical model, viscosity, crystallization temperature, computer program.

INTRODUCTION

In metallurgy, the vast majority of the processes of formation of the composition of the metal proceeds through the molten slag and, therefore, the interest in studying its various properties is understandable. The base system for metallurgical slags is the $CaO – SiO_2 – Al_2O_3$ system, which has been repeatedly studied for the needs of various industries. Its study continues to this day due to the discrepancy between the properties of slags of the same composition by different researchers. A similar remark concerns slags of the $CaO – SiO_2 – Al_2O_3 – MgO$ system [1].

Meanwhile, the facts of the positive effect of B_2O_3 on the quality of pellets [4 - 5], the smelting of ferroalloys [6], and the ability to prevent the silicate decomposition of highly basic slags [7] have been established. This means the need to obtain systematic data on the properties of boron-containing silicate systems in the form of diagrams and their mathematical models for the wider use of B_2O_3 in industry.

Due to the large volume of such works, it is advisable to use rational methods for studying multicomponent systems. One of them is the method of mathematical planning on a simplex, which makes it possible to build “composition-property” diagrams, create mathematical models of properties, evaluate experimental errors and the adequacy of the obtained models [8 - 12].

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USED METHODS AND RESULTS OF RESEARCH

To describe the dependence of viscosity on the composition of the slag, a model in the form of a reduced polynomial of the fourth degree was used. According to the plan matrix, 35 slags were experimentally studied. The experiments were carried out on an electrovibrational viscometer in molybdenum apparatus in a stream of purified argon in the temperature range of 1 473–1 923 K. Slags were prepared from chemical reagents of the “pure for analysis” brand. According to parallel experiments at the same point, the dispersion was determined. The adequacy of the resulting mathematical model was assessed by the Student’s criterion for five control points that are not included in the planning matrix.

The area of slags selected for investigation graphically represents a tetrahedron. Its first vertex (y_1) with coordinates wt.% 48,48 CaO and 51,52 Al_2O_3 is in the crystallization region of 12 $CaO·7Al_2O_3$, the second (y_2) with 52 CaO and 48 SiO_2 is in the eutectic region between $CaSiO_3$ and $Ca_3Si_2O_7$, the third (y_3) with 9,8 CaO, 70.4 SiO_2 and 19,8 Al_2O_3 - at the junction of the fields of tridymite, anorthite, wollastonite in the region of the triple eutectic present here, and the fourth (y_4) is located in the volume of the tetrahedron and has coordinates 30,4 CaO , 33,6 SiO_2, 16 Al_2O_3 and 20 B_2O_3. According to the composition of oxide melts, technological processes for the production of cast iron, ferrosilicon, cement clinker, ceramics and other industries are covered. Table 1 shows the experiment planning matrix.

The latter are calculated from the experimental values of viscosity at each point. Viscosity values in the model are presented in the form of its logarithms to obtain commensurate function values for different states of the slag melt (homogeneous, heterogeneous). The mathematical model obtained by the described method for calculating viscosity at a temperature of 1 773 K is as follows:

$$
\begin{aligned}
\lg\eta = &-0{,}195x_1 - 0{,}407x_2 + 1{,}250x_3 - 0{,}464x_4 + \\
&+ 3{,}203x_1x_2 - 0{,}547x_1x_3 - 0{,}589x_1x_4 + 0{,}473x_2x_3 - \\
&- 0{,}377x_2x_4 + 1{,}124x_3x_4 - 1{,}415x_1x_2(x_1 - x_2) + \\
&+ 4{,}309x_1x_3(x_1 - x_3) + 1{,}948x_1x_4(x_1 - x_4) - \\
&- 2{,}31x_2x_3(x_2 - x_3) + 1{,}147x_2x_4(x_2 - x_4) + \\
&+ 1{,}669x_3x_4(x_3 - x_4) - 9{,}548x_1x_2(x_1 - x_2)^2 + \\
&+ 10{,}372x_1x_3(x_1 - x_3)^2 - 3{,}52x_1x_4(x_1 - x_4)^2 + \\
&+ 0{,}312x_2x_3(x_2 - x_3)^2 - 2{,}465x_2x_4(x_2 - x_4)^2 + \\
&+ 0{,}014x_3x_4(x_3 - x_4)^2 + 39{,}515\,x_1^2x_2x_3 + \\
&+ 9{,}185\,x_1^2x_2x_4 - 26{,}24\,x_1^2x_3x_4 + \\
&+ 1{,}806\,x_2^2x_3x_4 - 61{,}898\,x_1x_2^2x_3 - \\
&- 1{,}516\,x_1x_2^2x_4 - 11{,}982\,x_1x_3^2x_4 - \\
&- 9{,}925\,x_2x_3^2x_4 - 0{,}740\,x_1x_2x_3^2 - \\
&- 20{,}402\,x_1x_2x_4^2 + 12{,}089\,x_1x_3x_4^2 - \\
&- 9{,}166\,x_2x_3x_4^2 - 33{,}838\,x_1x_2x_3x_4 \qquad (1)
\end{aligned}
$$

where x_1, x_2, x_3 and x_4 are, respectively, the contents of CaO, SiO_2, Al_2O_3, B_2O_3 pseudocomponents at the vertices of the simplex, fractions of one (Table 1).

Similar equations are also obtained for other temperatures.

The expression for determining the crystallization temperature of the slag melt from the composition has the form:

$$
\begin{aligned}
T_{cr.} = &\ 1\,420\,x_1 + 1\,520\,x_2 + 1\,345\,x_3 + 1\,219\,x_4 + \\
&+ 320x_1x_2 + 70x_1x_3 + 342x_1x_4 - 330x_2x_3 - 266x_2x_4 + \\
&+ 448x_3x_4 + 0x_1x_2(x_1 - x_2) + 120x_1x_3(x_1 - x_3) + \\
&+ 386{,}67x_1x_4(x_1 - x_4) + 333{,}33x_2x_3(x_2 - x_3) - \\
&- 594{,}67x_2x_4(x_2 - x_4) - 496x_3x_4(x_3 - x_4) - \\
&- 1\,173{,}33x_1x_2(x_1 - x_2)^2 + 2866{,}67x_1x_3(x_1 - x_3)^2 - \\
&- 1\,410{,}67x_1x_4(x_1 - x_4)^2 + 93{,}33x_2x_3(x_2 - x_3)^2 + \\
&+ 296x_2x_4(x_2 - x_4)^2 - 1\,728x_3x_4(x_3 - x_4)^2 + \\
&+ 7\,240\,x_1^2x_2x_3 + 10\,525{,}3\,x_1^2x_2x_4 + \\
&+ 533{,}33\,x_1^2x_3x_4 + 3\,402{,}67\,x_2^2x_3x_4 - \\
&- 15\,160\,x_1x_2^2x_3 - 10\,296\,x_1x_2^2x_4 + \\
&+ 6125{,}33\,x_1x_3^2x_4 - 7\,773{,}33\,x_2x_3^2x_4 + \\
&+ 6\,906{,}67\,x_1x_2x_3^2 - 3\,173{,}33\,x_1x_2x_4^2 - \\
&- 4\,210{,}67\,x_1x_3x_4^2 + 2\,328\,x_2x_3x_4^2 - \\
&- 43\,168\,x_1x_2x_3x_4 \qquad (2)
\end{aligned}
$$

Based on the developed models, a computer program was created, the window of which is shown in Figure 1. It is recommended to carry out numerical calculations using it, since it gives more accurate values of slag properties compared to diagrams. We emphasize further that for 5 or more component systems, the mathematical model is the only way to find properties, because they cannot be displayed graphically on a plane. The properties of 4-component systems on a plane can be shown in the form of cuts along any oxide. For the system under study, this was done using the developed computer program. Note that the content of the models is more complete than the diagrams shown below, since on the latter, as an example, sections are given for a maximum of 4 % B_2O_3, while the model makes it possible to calculate the viscosity of slags with B_2O_3 up to 20 %. A similar remark can be made about the temperature range.

In other words, the above diagrams are nothing more than an example, because a graphic representation of all the obtained material would require significant material costs.

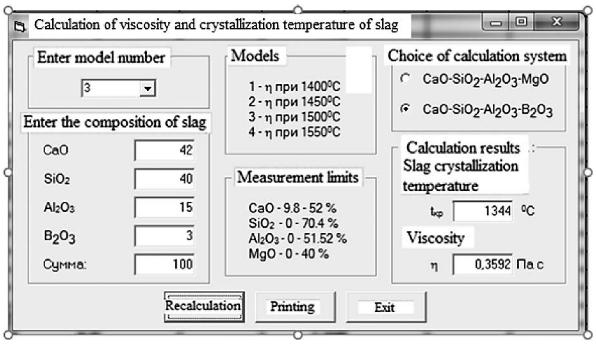

Figure 1 Window of the computer program

The diagrams below (Figures 2 and 3) are given in the form of isothermal sections for various boron oxide contents. For a comparable analysis, the figures also show the data of our own studies for the CaO – SiO_2 – Al_2O_3 and CaO – SiO_2 – Al_2O_3 – MgO systems [1].

Characterizing the general structure of these diagrams, it can be noted that they clearly show an extreme dependence of viscosity on the composition. In the CaO – SiO_2 – Al_2O_3 system, the most viscous are slags from the region of precipitation of triple eutectics with composition coordinates / %: 62 SiO_2; 14,7 Al_2O_3; 23,3 CaO and 70,4 SiO_2; 19,3 Al_2O_3; 9,8 CaO (Figure 2a). Due to the strong skeleton formation, the viscosity, even when overheated by more than 400 K, is 3–10 Pa·s. More mobile slags are contoured with 25-45 % SiO_2 and 45-50 % CaO, but they are high-temperature. The addition of 6 % MgO, common for blast furnace technology, expands the fields of fusible (1 623-1 673 K) (Figure 3b) and mobile (0,2–0,3 Pa·s) slags (Figure 2b). But when processing aluminous iron ores in blast furnaces, the formation of magnesian spinel MgO·Al_2O_3 makes slags refractory, which makes it difficult to obtain low-silicon cast irons for processing them into steel.

Table 1 **Experiment design matrix**

No	Slag composition							
	in code scale / share units				Wt / %			
	x_1	x_2	x_3	x_4	CaO	SiO_2	Al_2O_3	B_2O_3
1	1	0	0	0	48,48	-	51,52	-
2	0	1	0	0	52,00	48,00	-	-
3	0	0	1	0	9,80	70,40	19,80	-
4	0	0	0	1	30,40	33,60	16,00	20
5	1/2	1/2	0	0	50,24	24,00	25,76	-
6	1/2	0	1/2	0	29,14	35,20	35,66	-
7	1/2	0	0	1/2	39,44	16,80	33,76	10
8	0	1/2	1/2	0	30,90	59,20	9,90	-
9	0	1/2	0	1/2	41,20	40,80	8,00	10
10	0	0	1/2	1/2	20,10	52,00	17,90	10
11	3/4	1/4	0	0	49,36	12,00	38,64	-
12	3/4	0	1/4	0	38,81	17,60	43,59	5
13	3/4	0	0	1/4	43,96	8,40	42,64	-
14	0	3/4	1/4	0	41,45	53,60	4,95	5
15	0	3/4	0	1/4	46,60	44,40	4,00	5
16	0	0	3/4	1/4	14,95	61,20	18,85	-
17	1/4	3/4	0	0	51,12	36,00	12,88	-
18	1/4	0	3/4	0	19,47	52,80	27,73	15
19	1/4	0	0	3/4	34,92	25,20	24,88	-
20	0	1/4	3/4	0	20,35	64,80	14,85	15
21	0	1/4	0	3/4	35,80	37,20	12,00	15
22	1/2	1/4	1/4	0	25,25	42,80	16,95	-
23	0	0	1/4	3/4	39,69	29,60	30,71	5
24	1/2	1/4	0	1/4	44,84	20,40	29,76	5
25	1/2	0	1/4	1/4	34,29	26,00	34,71	5
26	0	1/2	1/4	1/4	36,05	50,00	8,95	-
27	1/4	1/2	1/4	0	40,57	41,60	17,83	5
28	1/4	1/2	0	1/4	45,72	32,40	16,88	5
29	1/4	0	1/2	1/4	24,62	43,60	26,78	5
30	0	1/4	1/2	1/4	25,50	55,60	13,90	-
31	1/4	1/4	1/2	0	30,02	47,20	22,78	10
32	1/4	1/4	0	1/2	40,32	28,80	20,88	10
33	1/4	0	1/4	1/2	29,77	34,40	25,83	10
34	0	1/4	1/4	1/2	30,65	46,40	12,95	5
35	1/4	1/4	1/4	1/4	35,17	38,00	21,83	

A more significant effect on improving the properties of slags can be achieved by adding B_2O_3 (Figures 2 and 3 positions c and d). This requires 1,5-3 times less boric anhydride than magnesium oxide. This is explained by the fragmentation of the silicon-oxygen skeleton of the slag as a result of the transition of boron from the 4th to the 3rd coordinated state with respect to oxygen at high temperatures and the formation of low-melting borates instead of refractory magnesia compounds.

For a comparable analysis, we experimentally studied the effect of MgO, CaF_2, and B_2O_3 additions on the viscosity of slag of the same composition (mass %): 40 CaO, 40 SiO_2, and 20 Al_2O_3 (Figure 4).

It can be seen that beyond 6-8 % MgO, the viscosity of the slag increases. This is not the case with CaF_2 and B_2O_3. Moreover, in terms of the effect on viscosity, B_2O_3 is superior to MgO, is not inferior to CaF_2, and is less environmentally hazardous than calcium fluoride.

CONCLUSION

Thus, on the basis of experimental studies using the simplex planning method, mathematical models of viscosity diagrams and crystallization temperatures of melts of the 4-component system CaO - SiO_2 - Al_2O_3 - B_2O_3 were created. Based on the models obtained, a computer program was created. When the user sets the composition of the slag from the control panel and starts the program, the program displays its viscosity in Pa·s and the crystallization temperature in ^{0}C. To visualize the properties of slags using the program, diagrams were constructed in the form of isothermal sections for boric anhydride.

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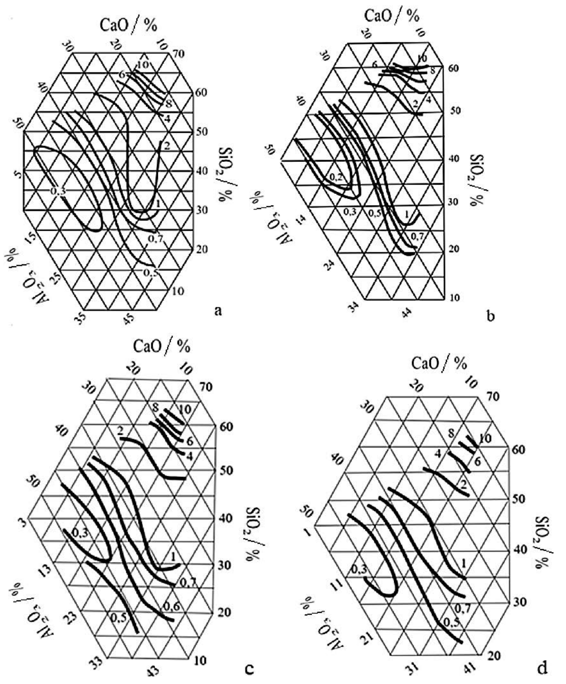

Figure 2 Diagrams of the viscosity of slags of the CaO – SiO_2 – Al_2O_3 system without additives (a), with 6 % MgO (b), 2 % B_2O_3 (c), 4 % B_2O_3 (d) at 1 823 K.

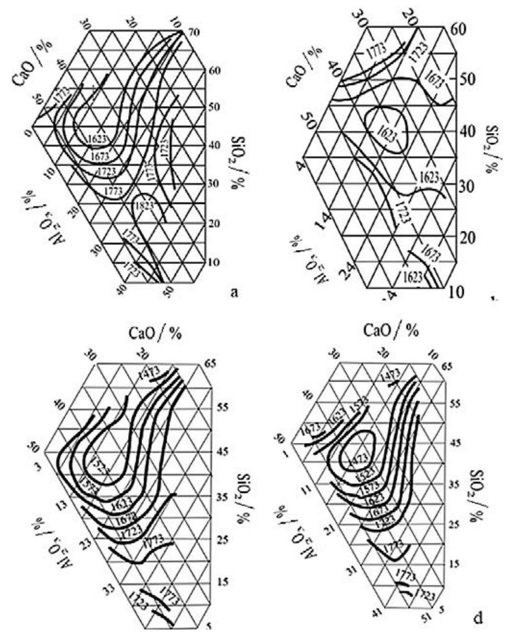

Figure 3 Diagrams of crystallization temperatures of melts of the CaO – SiO_2 – Al_2O_3 system without additives (a), with 6 % MgO (b), 2 % B_2O_3 (c), 4 % B_2O_3 (d).

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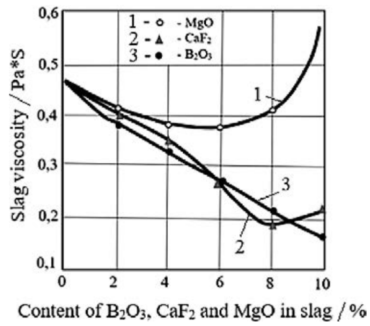

Figure 4 Comparative effectiveness of B_2O_3, CaF_2 and MgO influence on slag viscosity at 1 723 K

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Note: The responsible translator for English language is Nataliya Drag, Karaganda, Kazakhstan