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VISCOSITY AND ELECTRIC CONDUCTIVITY OF MELT SYSTEM OF CaO - Al_2O_3 - B_2O_3

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It was studied the viscosity and electric conductivity of the melt system CaO - Al_2O_3 - B_2O_3. On the base of experimental data it was created the mathematical model of studied features dependence on chemical structure of melt and temperature. There were created the computer programs which allow to calculate the temperature range at 1 823 – 1 973 K. There were constructed the triaxial diagrams based on models. It was found the reduction of viscosity and extension of electric conductivity of melt CaO - Al_2O_3 by adding B_2O_3.

Key words: metallurgy, CaO - Al_2O_3 - B_2O_3 system, viscosity, electric conductivity, axial diagram

INTRODUCTION

Melts of binary group CaO - Al_2O_3 have got wide circulation in the metallurgy by high purifying qualities. They are mostly used for deletion of sulfur from cast iron and different types of steel [1]. By adding oxidizers they successfully purify metal from phosphorous. Research of its physical characteristics have shown that the most optimum melts are which crystallized in a binary system CaO - Al_2O_3 at twelve-calcium seven aluminate (12 CaO·7 Al_2O_3) where it is easy to get fusible slags. However it should be noticed that they still have high temperature of crystallization and for better use of them it is required its overheating related to some expenses. That is why such fluxes as CaF_2, $CaCl_2$ and others are added [2]. It was noticed the expressed pass of fluorine and chlorine toxic compounds at the temperature of metallurgic redistribution [3].

They have decided to try boric anhydrite (B_2O_3) which has low temperature of melt (723 K) and which forms low temperature compounds with many oxides as an add to the melt CaO - Al_2O_3 [4]. It was planned to research viscosity and electric conductivity of triple system CaO - Al_2O_3 - B_2O_3.

WAYS OF RESEARCH

For measuring the viscosity it was used electrovibrator viscosimeter [5, 6]. It was graduated by heavy liquid (“Clerichy”) which has density close to the density of oxide melts. Reactionary crucible and viscosimeter probe were made of molybdenum. The temperature in working area of furnace fixed tungsten rhenium thermocouple BP-5/20 the end of which reinforced by alunite cover got to the bottom of crucible in a special dimple. Thermocouple was checked periodically by the temperature of pure metals melt.

Samples of slag were prepared from chemically pure reagents. At first they were fired then remelt and saved in the hermetic dish. The experiments were controlled at every point on the data of not less than three experiments by calculation of dispersion and root-mean-square error.

The experiments were held by mathematic planning at simplex [7 - 9] Figure1. For the research it was chosen the local part of triple diagram CaO - Al_2O_3 - B_2O_3 with coordinate peaks, mass %: y_1 = 62,20 CaO и 37,80 Al_2O_3; y_2 = 35,40 CaO и 64,60 Al_2O_3; y_3 = 42,00 CaO, 42,00 Al_2O_3 и 16,00 B_2O_3. (Table 1) According to recommendation [7-9] for description of triple system melt characteristics was chosen polynomial of fourth degree:

$$\begin{aligned}\lg\eta &= \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1x_2 + \\ &+ \beta_{13} x_1x_3 + \beta_{23} x_2x_3 + \gamma_{12} x_1x_2(x_1 - x_2) + \\ &+ \gamma_{13} x_1x_3(x_1 - x_3) + \gamma_{23} x_2x_3(x_2 - x_3) + \\ &+ \sigma_{12} x_1x_2(x_1 - x_2)^2 + \sigma_{13} x_1x_3(x_1 - x_3)^2 + \\ &+ \sigma_{23} x_2x_3(x_2 - x_3)^2 + \beta_{1123} x_1^2x_2x_3 + \\ &+ \beta_{1223} x_1x_2^2x_3 + \beta_{1233} x_1x_2x_3^2, \qquad (1)\end{aligned}$$

where

η – viscosity / Pa·sec,

β_1, β_2, β_3, γ_{12}, σ_{12}, and others – polynomial coefficients,

x_1, x_2, x_3 – fractions of unit according to the content of pseudocomponents CaO, Al_2O_3 and B_2O_3 at the peaks of simplex (Table 1).

Analogous equations were chosen for description pf electric conductivity of melts. In the matrix of plans recalculation of slag content from the coordinates of pseudocomponents into massive percentage were made by formulas:

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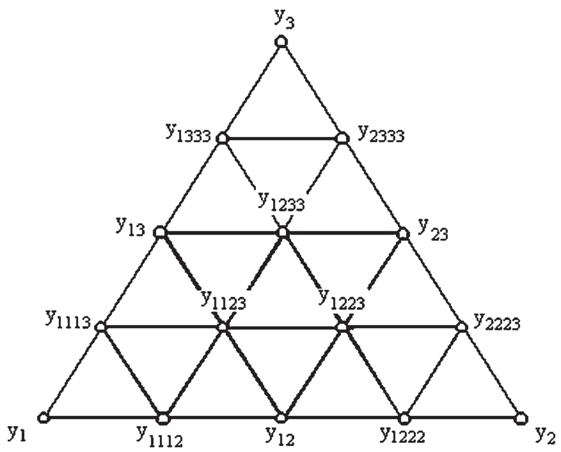


y1, y2, y3, - the vertices of the triangle
yi - designation of points plan

Figure 1 Disposition of experimental points at simplex

$$CaO = 62,2\ x_1 + 35,4\ x_2 + 42\ x_3, \quad (2)$$

$$Al_2O_3 = 37,8\ x_1 + 64,6\ x_2 + 42x_3, \quad (3)$$

$$B_2O_3 = 16\ x_3 \quad (4)$$

At the machine method of getting viscosity by the Formula (1) the system of equation (2-4) are solved according to x_1, x_2, and x_3:

$$x_1 = 0,0239{\cdot}CaO – 0,0131{\cdot}Al_2O_3 – 0,0283{\cdot}B_2O_3, \quad (5)$$

$$x_2 = -\ 0,014{\cdot}CaO + 0,0231{\cdot}Al_2O_3 – 0,0241{\cdot}B_2O_3, \quad (6)$$

$$x_3 = 0,0625{\cdot}B_2O_3 \quad (7)$$

Further, knowing the content of slag by CaO, Al_2O_3 and B_2O_3 using the formula (5-7) at first we get the value of x_1, x_2 and x_3 which we put to equation (1) it is get the value of viscosity.

According to chosen polynomial (equation 1) we have to get 15 experiments. Disposition of all the points at the triangle CaO - Al_2O_3 -B_2O_3 is shown in the picture 1 and its content at the weight % and coordinates of pseudocomponents (x_i) – at the matrix of plans (Table 1).

Table 1 **Matrix of experiment planning**

№	Melt content						Index of melt
	Code scale, fraction of units			weight / %			
	X_1	X_2	X_3	CaO	Al_2O_3	B_2O_3	
1	1	0	0	62,20	37,80	0	y_1
2	0	1	0	35,40	64,60	0	y_2
3	0	0	1	42,00	42,00	16	y_3
4	½	½	0	48,80	51,20	0	y_{12}
5	½	0	½	52,10	39,90	8	y_{13}
6	0	½	½	38,70	53,30	8	y_{23}
7	¾	¼	0	55,50	44,50	0	y_{1112}
8	¾	0	¼	57,15	38,85	4	y_{1113}
9	0	¾	¼	37,05	58,95	4	y_{2223}
10	¼	¾	0	42,10	57,90	0	y_{1222}
11	¼	0	¾	47,05	40,95	12	y_{1333}
12	0	¼	¾	40,35	47,65	12	y_{2333}
13	½	¼	¼	50,45	45,55	4	y_{1123}
14	¼	½	¼	43,75	52,25	4	y_{1223}
15	¼	¼	½	45,40	46,60	8	y_{1233}

RESULTS OF RESEARCH

Experimental values of viscosity at all 15 points of plan are in the Table 2. They are base for calculation of coefficients in the equation of polynomial (1). For example, β_1 = Igη$_1$; β_2 = lgη$_2$; β_{12} = 9/4(lgη$_{112}$ + lgη$_{122}$ - lgη$_1$·Igη$_2$) [9]. Thus all 15 coefficients of polynomial got by this way are given in the Table 3. Availability of coefficients let us define concretely the equation (1) for getting the value of viscosity at the temperature 1 823, 1 873, 1 923 and 1 973 K.

For example, at the temperature 1 873 K it looks as:

$$\lg\eta = -\ 0,1871\ x_1 – 0,167\ 5x_2 – 1\ x_3 – 1,2168\ x_1x_2 – 0,9214\ x_1x_3 –0,2182\ x_2x_3 – 1,1712\ x_1x_2(x_1– x_2) + 0,3768\ x_1x_3(x_1 – x_3) – -0,1496\ x_2x_3(x_2– x_3) – 2,3232\ x_1x_2(x_1 – x_2)^2 – -0,1037\ x_1x_3(x_1 – x_3)^2 + 1,5800\ x_2x_3(x_2– x_3)^2 – -4,9245\ x^2_1 x_2x_3 – 5,5091\ x_1 x^2_2x_3 +10,330\ x_1 x_2x^2_3 \quad (8)$$

Table 2 **Experimental value of viscosity**

№	Viscosity / Pa·sec			
	1 82 3K	1 873 K	1 923 K	1 973 K
y_1	1,60	0,65	0,30	0,17
y_2	9,95	0,68	0,39	0,28
y_3	0,13	0,10	0,08	0,07
y_{12}	0,47	0,33	0,23	0,17
y_{13}	0,19	0,15	0,13	0,10
y_{23}	0,28	0,23	0,20	0,17
y_{1112}	0,30	0,24	0,19	0,16
y_{1113}	0,36	0,30	0,25	0,22
y_{2223}	2,01	0,44	0,35	0,28
y_{1222}	0,59	0,39	0,26	0,18
y_{1333}	0,12	0,10	0,07	0,06
y_{2333}	0,23	0,18	0,15	0,13
y_{1123}	0,24	0,18	0,14	0,10
y_{1223}	0,29	0,23	0,18	0,14
y_{1233}	0,26	0,19	0,15	0,12

Table 3 **Coefficient of viscosity model**

№	Coefficient of polynomials	Coefficients of viscosity models at temperatures / K			
		1 823 K	1 873 K	1 923 K	1 973 K
1	β1	0,2041	- 0,1871	- 0,5229	- 0,7696
2	β2	0,9978	- 0,1675	- 0,4089	- 0,5528
3	β3	- 0,8861	- 1	- 1,0969	- 1,1549
4	β12	- 3,7154	- 1,2168	- 0,6896	- 0,4336
5	β13	- 1,5208	- 0,9214	- 0,3048	- 0,151
6	β23	- 2,4346	- 0,2182	0,2156	0,337
7	γ12	0,5496	- 1,1712	- 0,4224	0,3051
8	γ13	- 0,3627	0,3768	1,4176	1,9816
9	γ23	- 0,0024	- 0,1496	0,128	0,172
10	σ12	- 5,98	- 2,3232	- 1,2352	- 0,5931
11	σ13	- 1,1968	0,1037	- 0,2443	1,0851
12	σ23	4,9725	1,5800	1,5483	1,5192
13	β1123	1,7661	- 4,9245	- 11,115	- 19,034
14	β1223	- 9,0139	- 5,5091	- 4,9627	- 1,9299
15	β1233	19,195	10,3301	11,2304	12,9173

The equations are analogous at other temperatures. Thus the problem of creation the mathematical model can be considered solved. On the base of these models the computer program was created which shows at the screen and prints the value of viscosity at the values of melt and temperature given by desk. The program can be used at the range of melts and temperatures shown in the Table 1.

The electric conductivity of melt CaO - Al_2O_3 - B_2O_3 was studied. The current-voltage scheme realized on the combined set on viscosity measure by vibration was used for that . It let us measure viscosity on two main parameters during the same experiment. One of the electrode was viscosimeter probe whereas the second was molybdenic glass where the probe of slag was set to. For reduction of polarization at the slag – electrode board the current of high frequency was used [10]. The vacuum tube generator was used as a source of it. The cell was graduated by electrolyte which has electric conductivity close to studied melts: by melt $CaCl_2$ at 1 273 K, by melt KCl at 1 123 K and by one normal melt KCl at 293 K [11]. The experiments were planned mathematically and held at the 15 points where viscosity was studied (Table 4).

Table 4 **Experimental value of electric conductivity**

Melt index	Electric conductivity / χ $Ом^{-1} \cdot см^{-1}$			
	1 723 K	1 773 K	1 823 K	1 873 K
y_1	0,28	0,42	0,59	0,83
y_2	0,11	0,19	0,30	0,47
y_3	0,65	0,91	1,23	1,74
y_{12}	0,22	0,32	0,46	0,65
y_{13}	0,47	0,68	0,93	1,32
y_{23}	0,22	0,33	0,47	0,68
y_{1112}	0,21	0,35	0,51	0,76
y_{1113}	0,62	0,87	1,17	1,58
y_{2223}	0,11	0,19	0,31	0,50
y_{1222}	0,13	0,23	0,36	0,59
y_{1333}	0,54	0,76	1,05	1,41
y_{2333}	0,40	0,58	0,81	1,15
y_{1123}	0,43	0,62	0,85	1,20
y_{1223}	0,29	0,42	0,58	0,81
y_{1233}	0,36	0,51	0,71	0,98

The coefficients of polynomials were found experimentally by the values of electric conductivity in the above scheme (1). Its values are in the Table 5. They allow to derive mathematical equation for values of electric conductivity (χ) depending on the content at four temperatures : 1 723, 1 773, 1 823 and 1 873 K. For example there is a mathematical model of value lgχ at the temperature 1 873 K:

$$lg\chi = -0,082\, x_1 - 0,3279\, x_2 + 0,2405\, x_3 + 0,0735\, x_1x_2 + 0,1719\, x_1x_3 - 0,4953\, x_2x_3 - 0,0634\, x_1x_2(x_1 - x_2) + 1,1378\, x_1x_3(x_1 - x_3) - 0,4133\, x_2x_3(x_2 - x_3) + 0,3799\, x_1x_2(x_1 - x_2)^2 + 1,3685\, x_1x_3(x_1 - x_3)^2 + 0,3493\, x_2x_3(x_2 - x_3)^2 + 6,2068\, x^2_1 x_2x_3 + 4,0646 x_1 x^2_2 x_3 - 3,8796 x_1 x_2 x^2_3. \quad (9)$$

The check of conformity of got dependence was held on the criteria of Student at three extra control points (two experiments for every mix) at the level a = 0,05. Calculation has shown that in all cases $t_{exp.} = 3,267 < t_{tabl.} = 5,841$ that means the hypothesis of conformity is not rejected.

Table 5 **Coefficients of electric conductivity models**

№	Coefficients index	Coefficients of electric conductivity models at temperatures / K			
		1 723	1 773	1 823	1 873
1	β_1	- 0,5423	- 0,3729	- 0,2267	- 0,0820
2	β_2	- 0,9586	- 0,7212	- 0,5229	- 0,3279
3	β_3	- 0,1871	- 0,0410	- 0,0899	0,2405
4	β_{12}	0,3733	0,2110	0,1525	0,0735
5	β_{13}	0,1600	0,1685	0,1559	0,1719
6	β_{23}	- 0,3389	- 0,4015	- 0,4457	- 0,4953
7	γ_{12}	- 0,0312	0,0316	0,0112	- 0,0634
8	γ_{13}	1,3121	1,2284	1,1212	1,1378
9	γ_{23}	- 0,9328	- 0,7708	- 0,5906	- 0,4133
10	σ_{12}	- 2,1982	- 0,8527	- 0,4654	0,3799
11	σ_{13}	2,1772	1,8997	1,8515	1,3685
12	σ_{23}	- 0,8934	- 0,4804	- 0,0006	0,3493
13	β_{1123}	4,1398	4,6445	5,0029	6,2068
14	β_{1223}	11,5500	9,3388	6,7502	4,0646
15	β_{1233}	- 6,1681	- 5,6302	- 4,3851	- 3,8796

RESULTS DISCUSSION

Mathematical models of viscosity (8) and electric conductivity (9) can be used for values of melts features of current and planned industry as well as construction of graphical diagrams. In the Figures 2 and 3 you can see the example of these models use for such purposes.

Its analysis shows that at all the range of temperatures B_2O_3 has considerable positive influence on viscosity. There are wide areas of mobile melts (0,15 - 0,20 Pa·sec) which is important for stable work of industrial sets where there are variations of in-process materials. Reduction of viscosity level by adding boron oxide let us make processes at the low thermal level which saves the heat.

Boron anhydrite (B_2O_3) has influence on electric conductivity of melts CaO - Al_2O_3. It is necessary to know it while choosing transformer of electric furnaces working on the principle of electric resistance of slag melts.

B_2O_3 does not have such additional charge carriers as Mg^{2+}, Ca^{2+}, F^-, O^{2-}, for example as manganese oxide and calcium fluoride because it is located as anions of different degree in the melt.

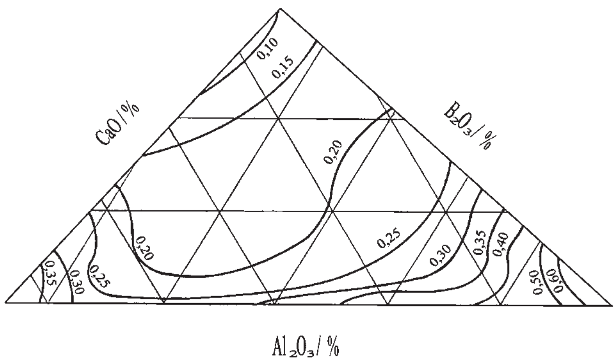
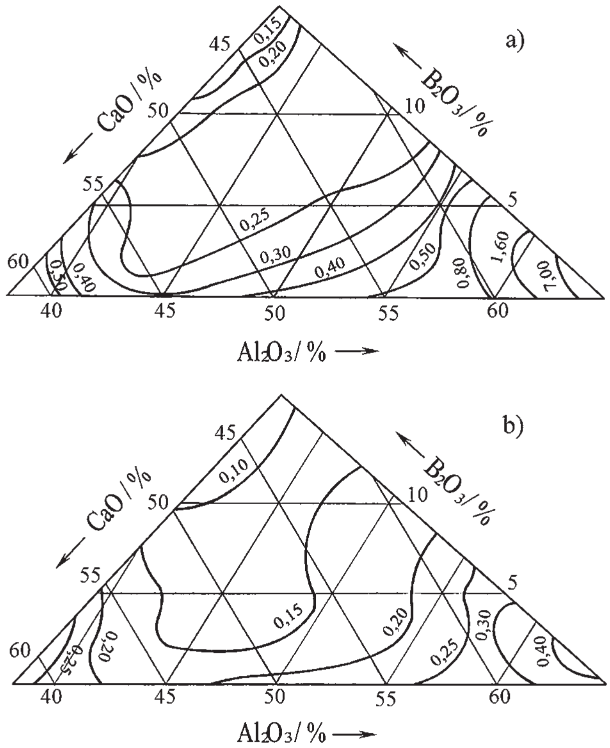


Figure 2 Diagram of melts viscosity of CaO - Al_2O_3 - B_2O_3 at 1 873 K



Figture 3 Diagrams of electric conductivity (values are increased 100 times) of melts CaO - Al_2O_3 - B_2O_3 for: a) 1 723; b) 1 823/K

Its influence is indicated by changing of melt viscosity. Transfer of the boron most part at high temperatures from four to three-coordinated state [12, 13] and occurrence of fusible borates [4] leads to reduction of melt viscosity that contributes to rise of charge carrier mobility.

The effect of its influence reduces in main liquid slags where there are many charge carriers (Ca^{2+}) and there are not any barriers (as in thick slags) for its drift. While reaching minimal values of viscosity the further admix B_2O_3 causes reduction of χ because of progressive reduction of charge carriers.

In metallurgy slags based on calcium aluminate are frequently used in such sets as "furnace-bucket" for deletion of sulfur and other contaminations whereas oxygen is deleted from the steel by admix for example Al and FeSi. We can get metal alloyage with boron by mix of deoxidizers and B_2O_3 while the concentration of boron is minimal (0,002 - 0,.003 %) and exceeds traditional ferroalloys ten times according to its positive influen. Thus we can see one more advantage of flux CaO - Al_2O_3 - B_2O_3 at fluorine and chlorine.

CONCLUSION

It was experimentally researched viscosity and electric conductivity of melts CaO - Al_2O_3 - B_2O_3. On the base of experimental data it was created the mathematical model of studied features dependence on chemical structure of melt and temperature. These models can be used for estimation of current melts features and planned for industries as well as for making graphical diagrams. It is shown that admix of boron anhydrite (B_2O_3) in the melt CaO - Al_2O_3 leads to reduction of viscosity and extension of electric conductivity. In the metallurgy melts CaO - Al_2O_3 - B_2O_3 can be used for deletion of sulfur from steel and its alloyage with boron.

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