EQUILIBRIUM BORON DISTRIBUTION BETWEEN FE–C–SI–AL MELT AND BORON-BEARING SLAG

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Abstract

HSC 6.1 Chemistry software (Outokumpu) and a simplex–lattice experiment design are employed in thermodynamic modeling of the equilibrium boron distribution between steel containing 0.1% C, 0.54% Si, and 0.01% Al (wt % are used throughout) and CaO–SiO_2–B_2O_3–25%Al_2O_3–8%MgO slag over a broad range of chemical composition at 1500 and 1600°C. For each temperature, mathematical models (in the form of a reduced third-order polynomial) are obtained for the equilibrium boron distribution between the slag and the molten metal as a function of the slag composition. The results of simulation are presented as graphs of the composition and equilibrium distribution of boron. The slag basicity has considerable influence on the distribution coefficient of boron. Experimental data practically confirm the results of thermodynamic modeling.

Keywords: *boron, steel, slag, interphase distribution, thermodynamic modeling, diagrams*

1. INTRODUCTION

It will be necessary to improve steel quality and reduce costs that the Russian steel industry is to remain competitive. The steel microalloying is one promising approach, which is widely used because it allows excellent mechanical properties to be obtained at low cost [1–3]. In particular, adding 0.001–0.005% boron permits increase in the strength of steel without loss of plasticity [2–3]. (Note that we assume wt% throughout.) As a rule, steel is microalloyed with boron by introducing boron-bearing ferroalloys in the melt. However, that increases the cost of the steel. An alternative is to obtain the boron used in microalloying by the reduction of boron-bearing oxide systems [4–5].

The present work focuses on the thermodynamic modeling of the equilibrium distribution of boron between the slag and the molten metal. Although the reactions in steel smelting are far from equilibrium, as a rule, it is important to know the reaction conditions for practical proposes. For example, on that basis, we may assess the behavior of boron in complex oxide and metallic phases; predict the optimal conditions for the production of steel of specified composition; and determine the best smelting technology.

2. MATERIALS AND METHODS

We use HSC 6.1 Chemistry software (Outokumpu) for thermodynamic modeling of the equilibrium boron distribution between the slag and the molten metal. That software is based on minimization of the Gibbs energy and variational thermodynamic principles [6]. In addition, a simplex–lattice experiment design is employed. Essentially, we derive a mathematical model relating the steel properties to the concentrations of the various mixture components [7–8].

In constructing the design matrix, constraints are imposed on the components of the CaO–SiO_2–B_2O_3–Al_2O_3–MgO system: 25% Al_2O_3; 8% MgO and 1-10% B_2O_3; the ratio CaO/SiO_2 = 2–5. As a result of the constraints on the system components, the region investigated may be represented by a local simplex in the form of two concentration triangles, whose vertices are pseudocomponents *Y*1, *Y*2, *Y*3, and *Y*4 (Fig. 1). Table 1 presents the design matrix.

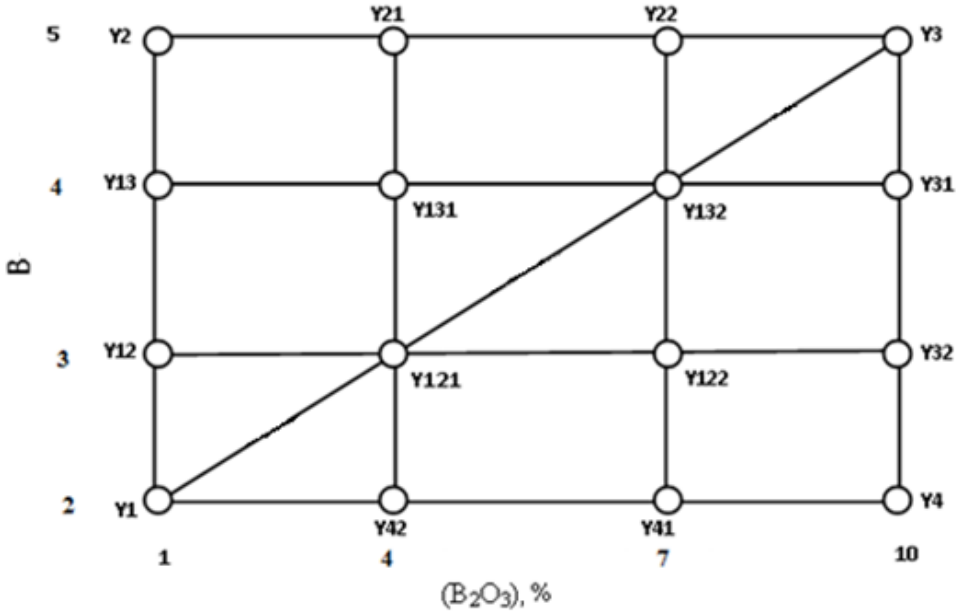


Fig. 1. The plan of a local simplex

Table 2 presents the results of thermodynamic modeling of the equilibrium boron distribution between the CaO–SiO_2–B_2O_3–25%Al_2O_3–8%MgO slag (corresponding to the 16 points in Table 1) and the molten steel containing 0.1% C, 0.54% Si and 0.01% Al. In modeling, we consider temperatures of 1500 and 1600°C. The working mass of the body is 100 kg (90% steel + 10% slag), with an air pressure of 0.1 MPa in the system.

The approximate model selected to describe the dependence of the equilibrium boron distribution between the slag and metal (LB) on the slag composition is a third-order polynomial, whose coefficients are calculated by means of the data in Tables 1 and 2. The corresponding equations take the following form.

For the concentration triangle $Y1Y2Y3$ of the local simplex, at 1500°C

$$L_B = 144x_1 + 97x_2 + 291x_3 - 21x_1x_2 + 167x_1x_3 + 104x_2x_3 - 1{,}1x_1x_2(x_1 - x_2) + 29x_1x_3(x_1 - x_3) + 35x_2x_3(x_2 - x_3) + 62x_1x_2x_3; \quad (1)$$

For the concentration triangle $Y1Y2Y3$ of the local simplex, at 1600°C

$$L_B = 179x_1 + 117x_2 + 354x_3 - 30x_1x_2 + 180x_1x_3 + 140x_2x_3 - 12x_1x_2(x_1 - x_2) + 73x_1x_3(x_1 - x_3) + 67x_2x_3(x_2 - x_3) - 53x_1x_2x_3; \quad (2)$$

For the concentration triangle $Y1Y4Y3$ of the local simplex, at 1500°C

$$L_B = 144x_1 + 381x_2 + 291x_3 + 191x_1x_2 + 167x_1x_3 + 2{,}3x_2x_3 - 28x_1x_2(x_1 - x_2) + 29x_1x_3(x_1 - x_3) + 29x_2x_3(x_2 - x_3) - 297x_1x_2x_3; \quad (3)$$

For the concentration triangle $Y1Y4Y3$ of the local simplex, at 1600°C

$$L_B = 179x_1 + 473x_2 + 354x_3 + 254x_1x_2 + 180x_1x_3 + 3{,}4x_2x_3 - 41x_1x_2(x_1 - x_2) + 73x_1x_3(x_1 - x_3) - 33x_2x_3(x_2 - x_3) + 52x_1x_2x_3, \quad (4)$$

№	Slag	Slag composition						
		In terms of pseudocomponents				In terms of initial components, wt %		
		X1	X2	X3	X4	CaO	SiO_2	B_2O_3
1	Y1	1	0	0	0	44.1	21.9	1
2	Y2	0	1	0	0	54.9	11.1	1
3	Y3	0	0	1	0	47.5	9.5	10
4	Y4	0	0	0	1	38.1	18.9	10
5	Y13	0,33	0,67	0	0	53.0	13.0	1
6	Y132	0,33	0	0,67	0	48.0	12.0	7
7	Y22	0	0,33	0,67	0	50.0	10.0	7
8	Y12	0,67	0,33	0	0	49.4	16.6	1
9	Y121	0,67	0	0,33	0	47.2	15.8	4
10	Y21	0	0,67	0,33	0	52.4	10.6	4
11	Y131	0,33	0,33	0,33	0	50.3	12.7	4
12	Y41	0,33	0	0	0,67	40.0	20.0	7
13	Y31	0	0	0,67	0,33	45.8	11.2	10
14	Y42	0,67	0	0	0,33	42	21	4
15	Y32	0	0	0,33	0,67	42.8	14.2	10
16	Y122	0,33	0	0,33	0,33	44.9	15.1	7

Table 1. Experiment-design matrix

Here $L_B = (B_2O_3)/[B]$ is the boron distribution coefficient between the slag and the steel; *xi* is the content of component *i* in the slag, in terms of the pseudocomponent coordinates.

The following formulas are employed to convert from the pseudocomponent coordinates (*xi*) to the coordinates of the initial components (wt %):

$$CaO = 44{,}1x1 + 54{,}9x2 + 47{,}5x3 + 38{,}1x4;$$

$$SiO_2 = 21{,}9x1 + 11{,}1x2 + 9{,}5x3 + 18{,}9x4;$$

$$B_2O_3 = x1 + x2 + 10x3 + 10x4.$$

№	Slag	1500°C			1600°C		
		[B]	(B_2O_3)	L_B=(B_2O_3)/[B]	[B]	(B_2O_3)	L_B=(B_2O_3)/[B]
1	Y1	0.007	0.978	143.8	0.0055	0.982	178.6
2	Y2	0.010	0.968	96.8	0.0083	0.973	117.3
3	Y3	0.034	9.891	290.9	0.028	9.910	353.9
4	Y4	0.026	9.916	381.4	0.021	9.932	473.0
5	Y13	0.009	0.971	107.9	0.0074	0.976	131.9
6	Y132	0.025	6.920	276.8	0.021	6.932	330.1
7	Y22	0.028	6.910	246.8	0.023	6.926	301.1
8	Y12	0.008	0.975	123.4	0.0065	0.979	150.6
9	Y121	0.017	3.945	232.1	0.014	3.955	282.5
10	Y21	0.021	3.932	187.3	0.017	3.945	232.1
11	Y131	0.019	3.939	207.3	0.016	3.948	246.8
12	Y41	0.020	6.936	346.8	0.016	6.948	434.3
13	Y31	0.031	9.900	319.4	0.025	9.920	396.8
14	Y42	0.015	3.952	263.4	0.012	3.961	330.1
15	Y32	0.028	9.910	353.9	0.023	9.926	431.6
16	Y122	0.023	6.926	301.1	0.018	6.942	385.7

Table 2. Results of thermodynamic calculation of the equilibrium boron content in the steel and its distribution between the slag and steel

We may regard Eqs. (1) – (4) as satisfactory at the 0.01 significance level. They may be used to calculate the equilibrium boron distribution coefficients between the CaO slag and the steel, which are used, in turn, to plot composition–property diagrams.

Experimental studies of the interfacial boron distribution between slag and metal were carried out at a high-temperature installation based on the Tamman resistance furnace. The slag of the $CaO–SiO_2–B_2O_3–25\%Al_2O_3–8\%MgO$ system was used as the experimental slag corresponding to the chemical composition of the point Y21 of the local simplex (see Table 1). Steel was used as the metal containing 0.1% carbon, 0.54% silicon and 0.01% aluminum. Metal sample mass 90 g and slag 9 g (10% of metal weight) was charged into a magnesian crucible and melted. The molten metal and slag were heated to temperature 1600°C and kept in a crucible for 10 to 30 minutes. Three experiments were conducted with holding the metal and slag in the crucible: for 10 min - experiment 1; 20 min - experiment 2 and 30 min - experiment 3.

3. RESULTS

We present the results as diagrams of the equilibrium boron distribution coefficients between the $CaO–SiO_2–B_2O_3–25\%Al_2O_3–8\%MgO$ slag and the steel at 1500°C (Fig.2) and 1600°C (Fig.3). The continuous curves are isolines of the equilibrium interphase boron distribution. The figures on the dashed curves are the values of the slag basicity (CaO/SiO2) to which they correspond.

The results of the laboratory experiment on the reduction of boron in the metal under the slag of the test compositions at 1600°C are shown in Fig. 4.

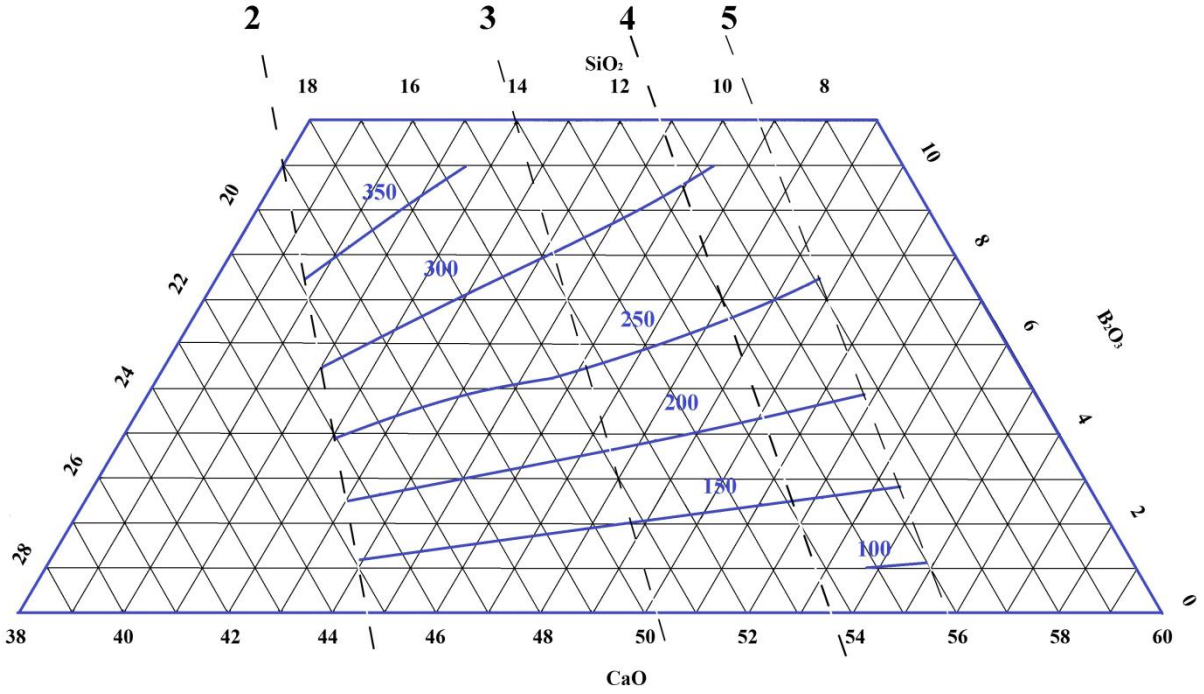


Fig. 2. Distribution of boron between CaO–SiO_2–B_2O_3–25%Al_2O_3–8% MgO slag and the steel at 1500°C when the basicity from 2 to 5.

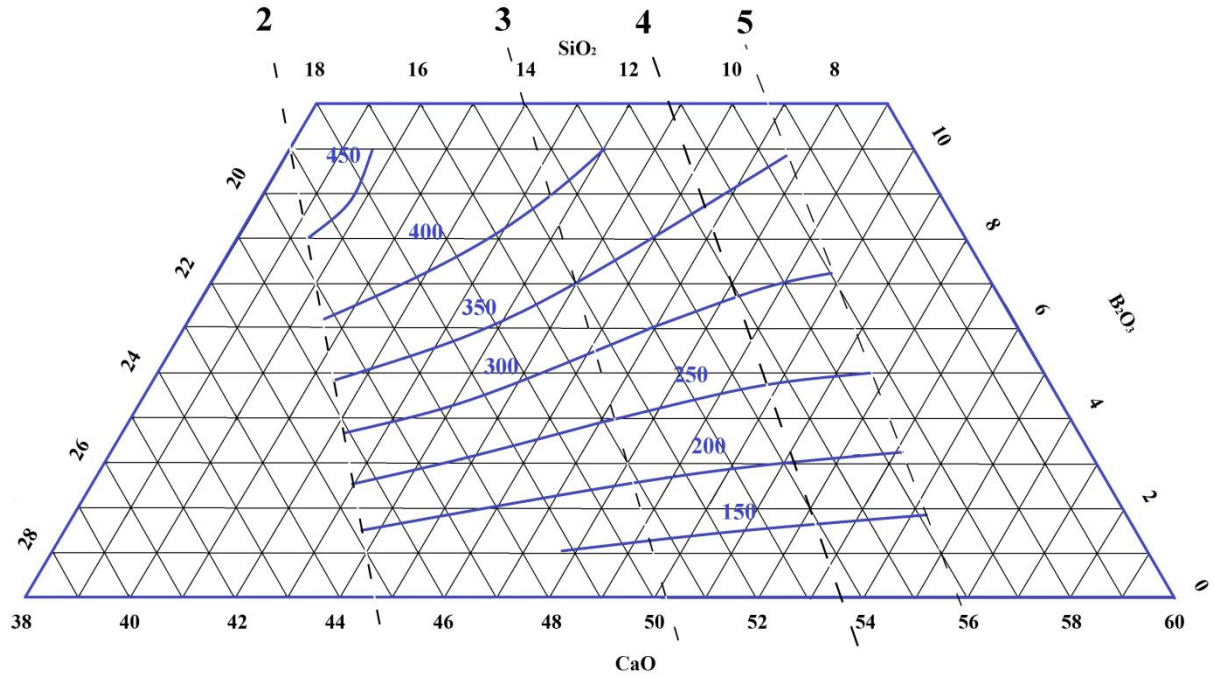


Fig. 3. Distribution of boron between CaO–SiO_2–B_2O_3–25%Al_2O_3–8% MgO slag and the steel at 1600°C when the basicity from 2 to 5.

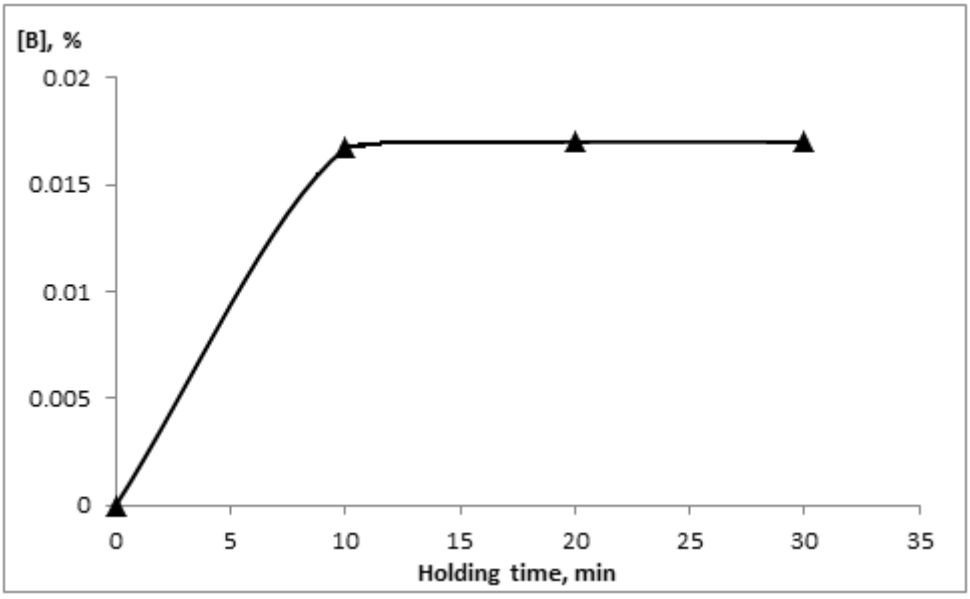


Fig. 4. Experimental boron content in the metal at exposure under slag $CaO–SiO_2–B_2O_3–25\%Al_2O_3–8\%$ MgO at 1600°C

4. DISCUSSION

Analysis of Figs. 2 and 3 permits quantitative assessment of how the steel temperature and chemical composition of the slag affect the boron distribution.

The equilibrium coefficient of boron distribution between metal and slag basicity 2-3 containing 6-10% B_2O_3 is at the level of 300-350 and decreases to 250-150 with decreasing concentration of B_2O_3 to 1-5% at a temperature of 1500°C. Slags of increased basicity to 3-5 are accompanied by a decrease in the equilibrium coefficient of interfacial boron distribution by an average of 50 in the investigated concentration range of B_2O_3 (1-10%) (Fig.2). This means that an increase of slag basicity has a positive effect on the development of the boron reduction process. Increasing the temperature to 1600°C is accompanied by a decrease in the degree of boron reduction. An increase in temperature by 100°C leads to an increase in the boron distribution coefficient by an average of 50 in the considered basicity range and the content of B_2O_3 in the slag (Fig. 3).

Exposure of steel containing 0.1% carbon, 0.54% silicon and 0.01% aluminum under a slag containing 52.4% CaO, 10.6% SiO2, 25% Al2O3, 8% MgO and 4% B2O3 is accompanied by boron reduction, which concentration approaches equilibrium after 10 minutes of exposure, reaches 0.017% B and practically does not change throughout the entire experiment. At the same time, experimental data practically confirm the results of thermodynamic modeling.

5. CONCLUSIONS

With minimum expenditure of time and materials, thermodynamic modeling and a simplex–lattice experiment design yield new information regarding the equilibrium boron distribution between steel containing 0.1% C, 0.54% Si, and 0.01% Al and $CaO–SiO_2–B_2O_3–25\%Al_2O_3–8\%$MgO slag over a broad range of chemical composition, at 1500 and 1600°C. This is confirmed by experimental data. We find that the slag basicity has considerable influence on the reduction of boron in the given composition range of the oxide and metallic phases.

The results of thermodynamic modeling and experimental data are of considerable practical importance. For example, by regulating the steel temperature and the slag composition, we may control the reduction of boron and predict its concentrations in the steel.

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