

# Influence of boric anhydride upon the physical and chemical properties of ferrosilicon slag

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**Abstract.** The authors study the influence of boric anhydride upon the physical and chemical properties of slag in the manufacture of ferrosilicon. It is established that adding boric anhydride to the slag changes its refractory quality and its viscosity and eases pouring slag and metal. Slags with optimal composition and properties are described.

## 1. Introduction

Influence of slag upon the process of ferrosilicon production significantly increases when chip included into the fusion material is partly replaced by ferriferous oxide materials, for example, mixed ore pellets or ores with high content of iron. In this case the amount of slag in relation to metal achieves 20%. In the furnace considerable part of metal formation processes involves the slag phase and that is why so much attention is drawn to studying its properties [1-6].

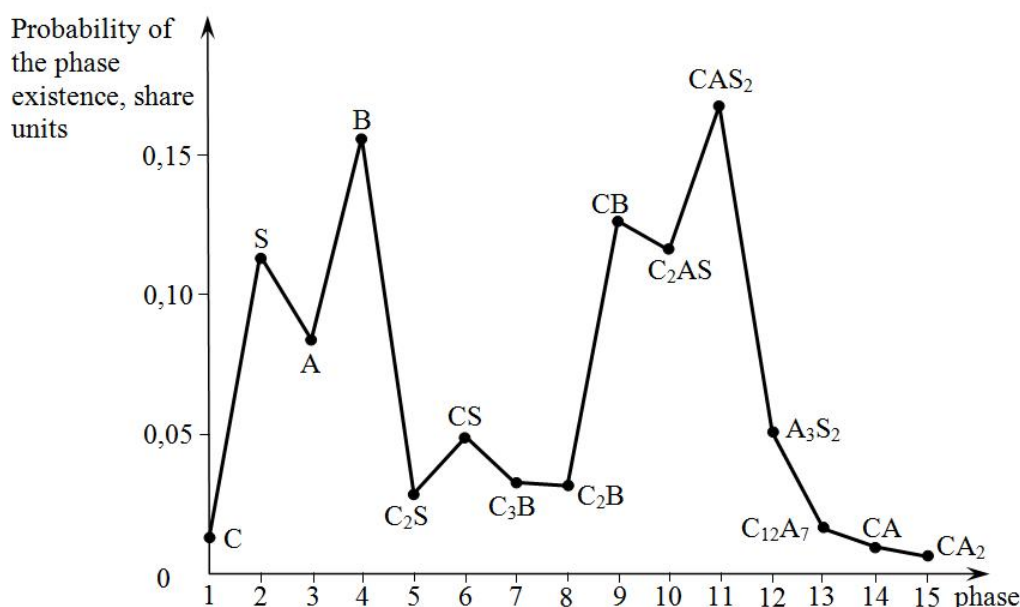
In work [7] the influence of fluorides adding upon the cinematics of interaction between  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  melts and silicon carbide (SiC) was studied. At the same time it is evident that the environmental hazard of fluorides calls forth the necessity of selecting other intensifiers. Borates are of interest in this context.

## 2. Theoretical basis

The most important characteristic of slags is their phase composition as it allows explaining many peculiarities of their physical properties. Most metallurgic slags are silicate, i.e they contain this or that amount of silice ( $\text{SiO}_2$ ). The system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ , is basic to describe the slag formation processes in the manufacture of ferrosilicon. The given system was studied many times to specify the boundaries of phase fields of various compounds. Reference literature presents methods of analytical description of phase equilibrium in complex systems when the amount of the phases formed is calculated according to mathematical formulas relating the phase composition to the chemical one [8, 9]. If boric anhydride is introduced into the fusion material, the slag formed can be described by the four-component system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ . The diagram of its phase composition is suggested in work [10]. To build the diagram of phase composition the authors used thermodynamically-diagrammatical method applying Gibbs energy minimization principle and regularities of construction of phasing diagrams. Application of the given method allowed dividing the four-component system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$  into four three-component subsystems including 18 elementary tetrahedrons of coexisting phases. Table 1 presents the consolidated characteristics of 15 main components of the given system.



Figure 1 provides the data on relative volume of tetrahedrons containing the studied phases called the probability of phase existence in the system of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ . The largest volume in this system is taken by anorthite ( $\text{CAS}_2$ ), boric anhydride ( $\text{B}_2\text{O}_3$ ) and silica. As all of them are acid it must be advantageous for ferrosilicon production which is completed with application of acid slags.



**Figure 1.** Probability of the phase existence in the system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ .

Table 2 presents specific compositions of slags from FS65 ferrosilicon production which are the result of not only transfer of some unreduced fusion mixture components into the oxide melt but also of fluxing stone addition to regulate the slag properties. It is easy to notice significant variety of slag composition resulting from insufficient optimality of slag fusion practice. Content of silica in the slags varies from 30 (slag 8) to 82.9% (slag 10), calcium oxide – from 6.32 (slag 7) to 32.69% (slag 2) and aluminium earth – from 13.47 (slag 10) to 44.02% (slag 5). Ratio  $\text{CaO/SiO}_2$  which characterizes the acid-base properties of slags is within 0.04-1.25.

On the base of phase composition diagram of  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$  system a mathematical model was developed allowing estimation of phase composition of slag on the base of its chemical composition. The calculation data (Table 2) show that production slags are crystallized in completely different areas of phase diagram where such phase components as anorthite, helenite ( $\text{C}_2\text{AS}$ ), mullite ( $\text{A}_3\text{S}_2$ ), corundum ( $\text{Al}_2\text{O}_3$ ), cristobalite (S) differ markedly in terms of their physical and chemical characteristics giving the slags the same differing properties which does not aid stable operation of the furnace. Some slags of stably low activity are in the phase triangle cristobalite-anorthite-mullite and even being heated up to 1750-1850°C have high viscosity, are badly poured from the furnace due to the carcass type of anion component structure of the first two phases.

Very rarely we can notice the cases of slag in the region of crystallization of helenite-anorthite-corundum. But we can clearly see the intention of technologists to fall into the optimal area of phase triangle anorthite-helenite-pseudowollastonite (CS) recommended by some researchers [11] where the slags are grouped at the confluence of anorthite and helenite. The composition of slag recommended in work [12] as optimal for ferrosilicon production is close to real ferroalloy slag 6 (Table 2) containing 37.39 %  $\text{SiO}_2$ , 36.13 %  $\text{Al}_2\text{O}_3$  and 26.48 %  $\text{CaO}$ . As phase components it includes 70.31 % of anorthite, 1.73 % of pseudowollastonite and 27.96 % of helenite.

**Table 1.** The consolidated characteristics of phases of system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>

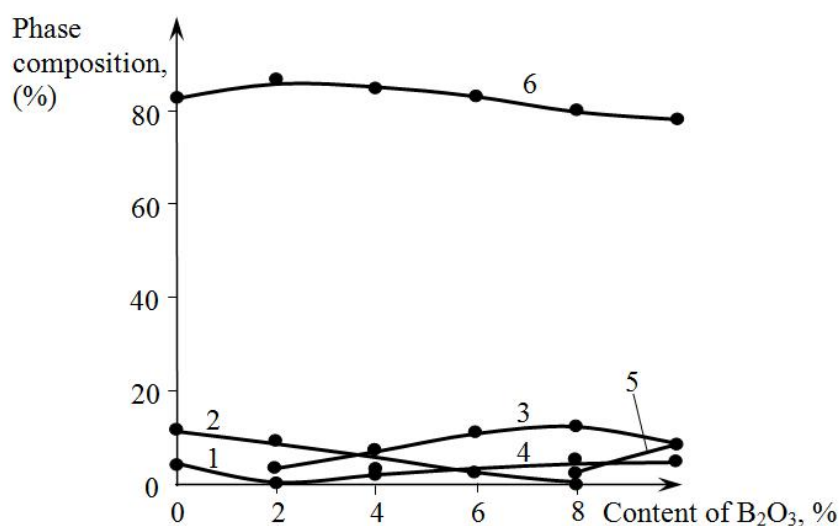
| №  | Phase                          | Composition, mas % |      |      |      | t <sub>melt.</sub> ,<br>°C | Polytopes, containing the phase |        |
|----|--------------------------------|--------------------|------|------|------|----------------------------|---------------------------------|--------|
|    |                                | C                  | S    | A    | B    |                            | amount                          | volume |
| 1  | C                              | 100                | 0    | 0    | 0    | 2625                       | 1                               | 0.0528 |
| 2  | S                              | 0                  | 100  | 0    | 0    | 1713                       | 3                               | 0.4591 |
| 3  | A                              | 0                  | 0    | 100  | 0    | 2050                       | 5                               | 0.3434 |
| 4  | B                              | 0                  | 0    | 0    | 100  | 450                        | 6                               | 0.6298 |
| 5  | C <sub>2</sub> S               | 65.1               | 34.9 | 0    | 0    | 2130                       | 5                               | 0.1155 |
| 6  | CS                             | 48.3               | 51.7 | 0    | 0    | 1544                       | 4                               | 0.1984 |
| 7  | C <sub>3</sub> B               | 70.6               | 0    | 0    | 29.4 | 1490                       | 7                               | 0.1343 |
| 8  | C <sub>2</sub> B               | 61.5               | 0    | 0    | 38.5 | 1310                       | 5                               | 0.1262 |
| 9  | CB                             | 44.4               | 0    | 0    | 55.6 | 1160                       | 7                               | 0.5076 |
| 10 | C <sub>2</sub> AS              | 40.9               | 21.9 | 37.2 | 0    | 1513                       | 12                              | 0.4706 |
| 11 | CAS <sub>2</sub>               | 20.2               | 43.2 | 36.6 | 0    | 1553                       | 7                               | 0.6742 |
| 12 | A <sub>3</sub> S <sub>2</sub>  |                    | 28.2 | 71.8 | 0    | 1910                       | 2                               | 0.2020 |
| 13 | C <sub>12</sub> A <sub>7</sub> | 48.65              | 0    | 51.5 | 0    | 1455                       | 2                               | 0.0661 |
| 14 | CA                             | 35.5               | 0    | 64.5 | 0    | 1605                       | 3                               | 0.0359 |
| 15 | CA <sub>2</sub>                | 21.6               | 0    | 78.4 | 0    | 1750                       | 2                               | 0.0230 |

**Table 2.** Chemical and phase composition of slags of FS65 alloy production.

| №  | Chemical, % |                  |                                | <u>CaO</u>                     | <u>CaO</u>       | Phase, %          |       |                  |       |                               |       |
|----|-------------|------------------|--------------------------------|--------------------------------|------------------|-------------------|-------|------------------|-------|-------------------------------|-------|
|    | CaO         | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | C <sub>2</sub> AS | CS    | CAS <sub>2</sub> | S     | A <sub>3</sub> S <sub>2</sub> | A     |
| 1  | 24.38       | 43.27            | 32.35                          | 0.75                           | 0.56             | 4.34              | 11.66 | 84.00            |       |                               |       |
| 2  | 32.69       | 30.35            | 36.96                          | 0.88                           | 1.08             | 60.31             |       | 39.69            |       |                               |       |
| 3  | 8.95        | 67.83            | 23.22                          | 0.39                           | 0.13             |                   |       | 44.30            | 45.94 | 9.76                          |       |
| 4  | 22.21       | 42.82            | 34.97                          | 0.64                           | 0.52             | 3.58              | 4.49  | 91.93            |       |                               |       |
| 5  | 18.75       | 37.23            | 44.02                          | 0.43                           | 0.50             | 4.39              |       | 83.95            |       |                               | 11.66 |
| 6  | 26.48       | 37.39            | 36.13                          | 0.73                           | 0.71             | 27.96             | 1.73  | 70.31            |       |                               |       |
| 7  | 6.32        | 61.93            | 31.74                          | 0.20                           | 0.10             |                   |       | 31.28            | 40.44 | 28.28                         |       |
| 8  | 37.64       | 30.00            | 32.36                          | 1.16                           | 1.25             | 67.02             | 12.67 | 20.31            |       |                               |       |
| 9  | 30.69       | 35.19            | 34.12                          | 0.90                           | 0.87             | 40.56             | 7.43  | 52.01            |       |                               |       |
| 10 | 3.63        | 82.90            | 13.47                          | 0.27                           | 0.04             |                   |       | 18.97            | 72.43 | 9.60                          |       |
| 11 | 29.30       | 32.80            | 37.90                          | 0.77                           | 0.89             | 45.53             |       | 52.82            |       |                               | 1.62  |

## Results and discussion

We applied the developed mathematical model to calculate the possible change of slag phase composition in case of adding boric anhydride into them. The results of calculation are presented in the graphical form in Figure 2. The calculation showed that, as the concentration of  $B_2O_3$  in slag increases, concentration of other substances reduces – that of helenite, anorthite, pseudowollastonite; at the same time formation of  $CaO \cdot B_2O_3$  (CB),  $CaO \cdot 2B_2O_3$  ( $CB_2$ ) and free silica (S) is observed being the result of typical for the given conditions reaction  $CaO \cdot SiO_2 + B_2O_3 = CaO \cdot B_2O_3 + SiO_2$ . Formation of low-melting calcium borates in slag (Table 1) opens up an opportunity of regulating its refractory quality and viscosity and free silica allows better reduction of silicon. To check the given calculations experimentally we completed a special study.



**Figure 2.** Influence of boric anhydride upon the phase composition of slag in ferrosilicon production: 1 –  $C_2AS$ , 2 –  $CS$ , 3 –  $CB$ , 4 –  $S$ , 5 –  $CB_2$ , 6 –  $CAS_2$ .

Viscosity of slag was estimated with electrovibrating Stengelmeyer viscosimeter in molybdenum melting pots with inner diameter of 20 and height of 35 mm. Diameter of spindle was 2.5 mm and depth of its immersion into the liquid melt was  $10 \pm 0.5$  mm. The temperature of slag was read by the thermal couple PR 30/6 which measuring junction was led to the bottom of the melting pot through a special sinking. Viscosity was measured in Tamman vertical tube furnace. Microscrew hoist was used to immerse the spindle to suitable depth.

The research showed that production slag which compositions are presented in Table 2 demonstrate unfavorable temperature dependence of viscosity. Slag 3 is highly viscous both in the furnace and when tapping even under considerable overheating. Under 1600-1650°C its viscosity is over 10 Pa·s (100 poise) which makes its tapping difficult. It is determined by such phases as tridymite (45.94%) and anorthite (44.30%) having carcass structure of anion component. Slag 8 is too base ( $CaO/SiO_2 = 1.25$ ), silicon is not reduced well from it, it is fused within a narrow temperature range, with unstable characteristic. It is situated in the region of high-melting helenite (67.02 %) and is not typical for FeSi production as well as

slag 3 ( $\text{CaO/SiO}_2 = 0.13$ ). Presence of slags with such composition and characteristics means that the process is not well proven.

The properties of another group of slags (№№ 1,2,6 и 9) are close to each other. They are suitable for normal working conditions. But slags 2 and 9 are characterized by slightly increased basicity and higher viscosity. Their characteristics can be improved by adding boric anhydride. Bor-containing slag retains high mobility which guarantees its easy tapping from the furnace and clean runner and slag pots. Slag 6 has the best characteristics of all production slags (Table 2). It has the lowest viscosity and is stable in terms of this characteristic within a wide temperature range. Slag 6 is received after adding limestone to the fusion material as in the other case it would be acid and situated deeper in the region of anorthite crystallization.

To improve its characteristics we added a varying amount of borate ore (but not the increased amount of limestone) to basic slag 5. The compositions of the studied slags are presented in Table 3.

Slags 12, 13, 14 were received by adding 5, 10 and 15 % of borate ore and slags 15, 16 and 17 – by adding 1, 2, 4 and 6% of  $\text{B}_2\text{O}_3$  to slag 5. With addition of borate ore into slags, together with increase of  $\text{B}_2\text{O}_3$  content ratio of  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  also grows. That's why borate ore can be regarded as complex flux. So, 1% of  $\text{B}_2\text{O}_3$  in the slag due to borate ore addition, ratio of  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  increases by 0.07-0.08 units. It has a significant influence upon slag viscosity. Thus, under the temperature of  $1500^\circ\text{C}$  the initial slag has viscosity of 5.3 Pa·s. Addition of 10% borate ore into it leads to viscosity decrease up to 3.2 Pa·s and content of  $\text{B}_2\text{O}_3$  in it is 0.76%. To produce slag with optimal composition and properties it is necessary to maintain the content of  $\text{B}_2\text{O}_3$  in it of about 1-2% by adding borate ore. The experimental data demonstrate that in this case the crystallization temperature of slags will be within  $1500\text{-}1550^\circ\text{C}$  and it is enough to overheat them up to  $1600\text{-}1650^\circ\text{C}$  to achieve viscosity of 1.0 Pa·s which is optimal for tapping from the furnace.

**Table 3.** Compositions of experimental slags

| №  | Proportion of ingredients, % |                  |                                |                               |      |                                    |                      |
|----|------------------------------|------------------|--------------------------------|-------------------------------|------|------------------------------------|----------------------|
|    | CaO                          | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | B <sub>2</sub> O <sub>3</sub> | MgO  | CaO/Al <sub>2</sub> O <sub>3</sub> | CaO/SiO <sub>2</sub> |
| 5  | 18.75                        | 37.23            | 44.02                          | -                             | -    | 0.43                               | 0.50                 |
| 12 | 19.50                        | 36.70            | 43.00                          | 0.39                          | 0.38 | 0.45                               | 0.53                 |
| 13 | 20.15                        | 36.26            | 42.10                          | 0.76                          | 0.73 | 0.48                               | 0.56                 |
| 14 | 20.80                        | 35.82            | 41.21                          | 1.11                          | 1.07 | 0.50                               | 0.58                 |
| 15 | 18.57                        | 36.86            | 43.58                          | 0.99                          | -    | 0.43                               | 0.50                 |
| 16 | 18.39                        | 36.50            | 42.33                          | 1.96                          | -    | 0.43                               | 0.50                 |
| 17 | 18.03                        | 35.80            | 42.33                          | 3.85                          | -    | 0.43                               | 0.50                 |
| 18 | 17.69                        | 35.13            | 41.53                          | 5.66                          | -    | 0.43                               | 0.50                 |

Formation of free-running slag in the presence of boric anhydride creates favorable kinematic conditions for reduction of silicon into metal due to surface renewal resulting from washing the products (SiC) of interaction between the reducing agent and the silica. Silicon carbide can react not only with silica with formation of silicon and carbon monoxides, but also with  $\text{B}_2\text{O}_3$  in slag with boron carbide and silicon monoxide formation leading to silicon

reduction and preventing excessive carbide forming especially when producing high-grade ferrosilicon.

### Conclusion

1. When we introduce boric anhydride ( $B_2O_3$ ) into production slags their composition includes low-melting calcium borates allowing changing their refractory quality and viscosity to optimize the process and ease taping of cast products.

2. Adding boric anhydride to the slags during ferrosilicon production promote process acceleration of silicon carbide destruction and reduces the diffusion barrier of silica reduction by silicon carbide.

3.  $B_2O_3$  as a stronger acid oxide displaces  $SiO_2$  in the compounds which increases its activity and more complete transfer into metal.

4. It is recommended to establish the borate ore consumption in the amount of receiving 1-2% of  $B_2O_3$  in the slag increasing it when carbide content in the furnace increases and in case of tight furnace operation due to excessive  $SiO_2$  in the slag.

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