THERMODYNAMIC MODELING OF THE BORBARIUM FERROALLOY SMELTING TECHNOLOGICAL PROCESS

A complete thermodynamic modeling of chemical transformations during carbothermic reduction of barium and boron from oxides has been performed. It was shown that during the processing of charge with a high BaO: BaO:B_2O_3(3:1), barium carbide (BaC_2), iron boride (FeB), and barium hexaboride (BaB_6) are present as phase components in the smelting products, with the former predominantly noticeable. The data obtained allow us to conclude that it is possible to produce a new ferroalloy containing boron and barium.

Key words: ferroalloy, thermodynamic modeling, barium, boron, phases.

INTRODUCTION

Boron and barium are effective alloying and modifying elements [1 - 4]. Boron alloys are produced predominantly in the form of ferroboron containing from 6 to 17 % boron. It is smelted in an expensive aluminothermic process due to the use of pure boric anhydride and aluminum metal as a reducing agent [5,6]. The most common barium alloy is silicobarium, produced from natural barite ores in a carbothermic manner [7,8].

Ferroboron in Kazakhstan is not produced, it is bought in foreign countries and used for smelting high - quality steels at metallurgical and engineering enterprises of the republic. Silicon barium was first produced in the CIS at the Ermakovsky (now Aksusk) ferroalloy plant in Kazakhstan using its own barite ores and coke [9]. But the volumes of its smelting are significantly inferior to those of traditional ferroalloys (ferrochrome, silicomanganese, ferrosilicon) and are produced if orders are available. This is apparently due to insufficient knowledge of the behavior of barium in steel and its limited use for low-silicon steels, since silicobarium contains up to 60 – 65 % Si.

In this work, it studied the possibility of producing a ferroalloy, simultaneously containing boron and barium, which can be called borbarium. It was believed that the presence of boron and barium, which have a positive effect on the properties of ferrous and non-ferrous metals, will allow the new ferroalloy to have a high demand for industry.

METHODS

At the first stage, a theoretical justification of the process was planned. For this, a complete thermodynamic simulation of the technology was performed. This approach is widely used to create new technologies and materials [10 - 14]. In this work, for these purposes, it was used the TERRA complex developed at the MVTU named after Bauman [15]. It allows to discover the chemistry of transformations in a wide range of compositions, temperatures, and pressures. Correct execution of the calculations requires the list of the complex and the thermodynamic properties of the process participants in the base of the complex. To establish them by the method of thermodynamic diagram analysis [16 - 18] it was created a phase diagram showing the possible compositions of the alloys planned for production (Figure 1). It was taken into account that with the adopted carbon thermal process, Fe, Ba, and B can form carbides, and barium and boron can form barium hexaboride BaB_6.

Using our own method [19,20], they are created a mathematical model of the diagram, which allowed us to carry out numerical calculations of the phases formed. A joint examination of the diagram and the mathematical model allows us to establish that the binary FeB - BaB_6, BaB_6 - BaC_2, BaC_2 - FeB, and B_4C - BaB_6 binary systems ensure the simultaneous presence of barium and boron in the ferroalloy, while the FeB - B_4C - system only contains boron. By varying the phase ratios in these systems, ferroalloys with different contents of barium and boron can be obtained. This approach allows to select ferroalloys for various alloyed metals (steel, cast iron, aluminum).

The oxide part of the charge for the production of ferroalloy was formed on the basis of the system state diagram BaO-B_2O_3[21]. The iron in the charge was set

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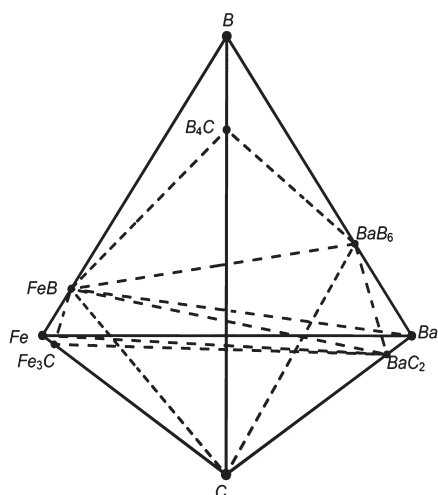
Figure 1 – System phase diagram Fe – Ba – B – C

in the form of metal shavings (Fe) in order to form iron borate, traditional for metallurgy, in a ferroalloy (FeB). The amount of carbon was set from the need for complete reduction of boron and barium from oxides. The calculations were carried out in the temperature range 273 – 3 000 K in increments of 50 degrees at a pressure in the system of 0,1 MPA.

RESEARCH RESULTS AND THEIR ANALYSIS

The charge 1 prepared for the study contained (in grams): 58,29 BaO, 8,83 B_2O_3, 13,42 Fe and 18,79 C. This selection of components made it possible to arrange the oxide part of the charge in the high - temperature level of the state diagram BaO - B_2O_3. The calculation results are presented graphically in Figure 2, a.
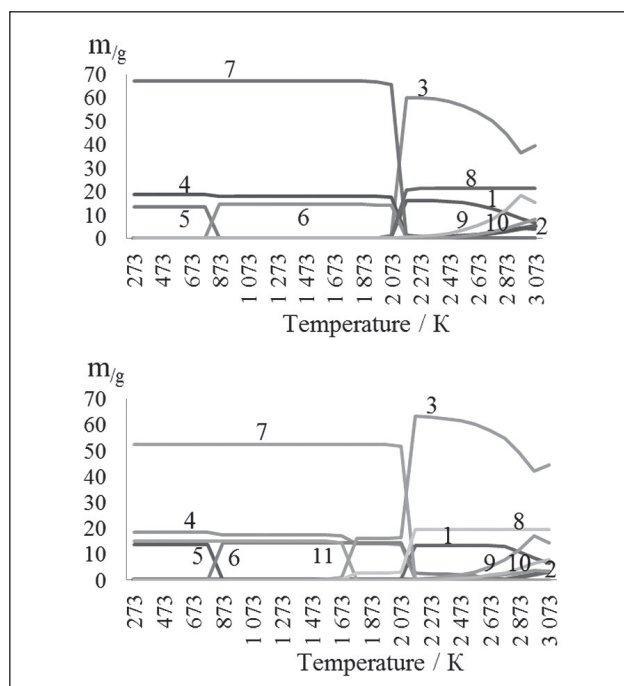

Figure 2 The composition of the products of the charge smelting 1(a) and 2(b)
1 - FeB, 2 - BaB_6, 3 - BaC_2, 4 - C, 5 - Fe, 6 - Fe_3C, 7 - $Ba_3B_2O_6$, 8 - CO_{gas}, 9 - Ba_{gas}, 10 - Fe_{gas}, 11 - BaO_{slag}

It can be seen that before the start of the reduction processes, the interaction of barium and boron oxides in the mixture leads to the formation of barium orthoborate $Ba_3B_2O_6$. The first product of the carbon thermal process is iron carbide, produced by the reaction $3\,Fe + C = Fe_3C$ (1). This can be seen by the loss in the charge of the amount of free Fe and C (figure 2,a). It emerges at 823 K in an amount of 0,14 mass fractions. Such its concentration remains unchanged up to 1 273 K, decreasing with a further increase in temperature to zero to 2 223 K. The amount of $Ba_3B_2O_6$ remains unchanged to high temperatures (Figure 2, a). The BaO and B_2O_3 contained in it do not react with carbon or Fe_3C due to the bound state, when their activity is reduced. Only beyond 2 000 K, its amount is intensively reduced. The probable cause of this may be a reaction $3\,Ba_3B_2O_6 + 2\,Fe_3C + 34\,C = 9\,BaC_2 + 6\,FeB + 18\,CO$ (2). After the exhaustion of iron carbide, the reduction process is carried out due to carbon $Ba_3B_2O_6 + 6\,C = 2\,BaC_2 + BaB_2O_4 + 18\,CO$ (3). These two reactions contribute to a rapid increase in concentration BaC_2. The emersion of barium hexaboride refers to a temperature of 2 273 K in an amount of 0.004 mass fractions, when BaB_2O_4 metaborate is involved in the reaction: $3\,BaB_2O_4 + 16\,C = BaB_6 + 2\,BaC_2 + 12\,CO$ (4) The maximum amounts of FeB (0.16 mass fractions) and BaC_2 (0.6 mass fractions) are observed at 2 273 K, and BaB_6 (0,04 mass fractions) at 3 023 K. The dominant phase of the processing of this mixture is barium dicarbide. The temperatures of occurrence and maximum content of BaC_2 found by calculation are higher than those observed during the reduction of barium from free oxide by the reaction $BaO + 3\,C = BaC_2 + CO$ (5). The calculation at the TERRa complex of the charge processing according to reaction (5) from one mole of barium oxide and three moles of carbon shows the emersion of BaC_2 already at 1 473 K in an amount of $0,18\cdot10^{-3}$ mass fractions. BaC_2 reaches its maximum value (0,85 mass fractions) at 1 823 K, and not at 2 273 K as during reduction from $Ba_3B_2O_6$. A similar phenomenon occurs during carbothermic reduction of boron from free oxide.

The reason is the decreased activity of boron and barium oxides in barium borate $Ba_3B_2O_6$ due to their bound state. Barium reduction can be facilitated from a charge in the quasi-binary $Ba_3B_2O_6$ - BaO system due to the presence of free barium oxide in it. An example of melting such a mixture (2) of 60,57 BaO, 6,88 B2O3, 13,44 Fe and 18,38 C is shown in the figure 2,b. Here BaC_2 emerges at 1 473 K, but already in an amount of $0,23\cdot10^{-3}$ mass fractions. At the temperature of 1 773 K, there is an intensive increase in the amount of BaC_2 (up to 0,16 mass fractions) and a decrease in BaO to zero. Since then, $Ba_3B_2O_6$ is involved in the reduction process, providing a further increase in concentration of BaC_2. Its maximum amount (0,63 mass fractions) falls on 2 223 K. FeB emerges at 2 023 K in an amount of $0,14\cdot10^{-3}$ mass fractions with a further increase in its concentration with increasing temperature (Figure 2,b).
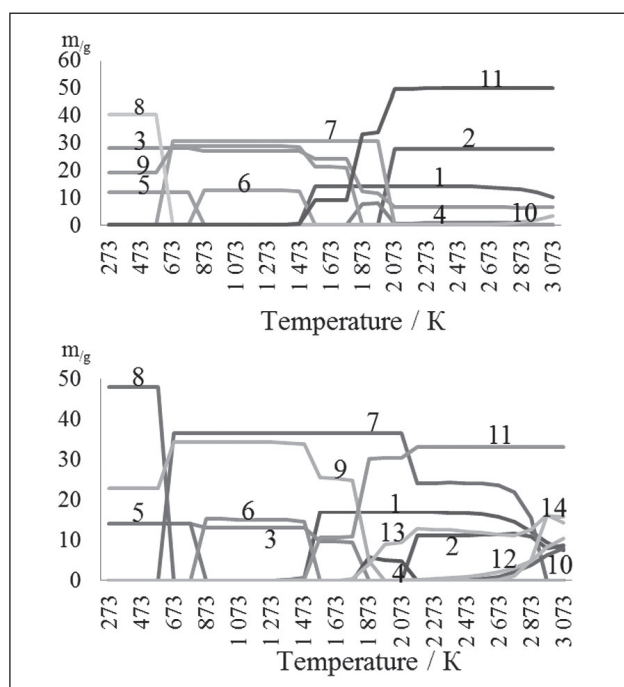
Figure 3 The composition of the melting products of the charge 3(a) and 4(b).
1 - FeB, 2 - BaB_6, 3 - C, 4 - B_4C, 5 - Fe, 6 - Fe_3C, 7 - BaB_2O_4, 8 - BaB_4O_7, 9 - B_2O_3, 10 - Fe_{gas}, 11 - CO_{gas}, 12 - BO_{gas}, 13 - B_2O_{2gaa}, 14 - Ba_{gas}

Barium hexaboride is formed in small quantities due to the early consumption of barium and boron oxides on the formation of BaC_2 and FeB.

A similar approach can be used to facilitate the reduction of boron of the fusible mixture (3) in the quasi-binary system $BaB_4O_7 + B_2O_3$ (Figure 3).

The presence of free B_2O_3 and obtained as a result of conversion at low temperatures according to the scheme $BaB_4O_7 = BaB_2O_4 + B_2O_3$ (6) promotes the reaction $3 B_2O_3 + 2 Fe_3C + 7 C = 6 FeB + 9 CO$ (7). The temperature of the highest FeB content (0,14 mass fractions) is much lower (1 623 K) than when it was obtained from $Ba_3B_2O_6$ (2 273 K), which reflects the difference in B_2O_3 activity in the initial oxides. The latter is present in the mixture to high temperatures, which contributes to the formation of boron carbide by reaction $2 B_2O_3 + 7 C = B_4C + 6 CO$ (8). After B_2O_3 is used, barium metabolite is involved in the reaction $BaB_2O_4 + 3 C + B_4C = BaB_6 + 4 CO$ (9). A temperature of 2 223 K accounts for a sharp decrease in the amount of C, B_4C, BaB_2O_4 and the emersion of BaB6 (Figure 3). With this charge, BaC_2 is absent in the smelting products. From the presented data it can be seen that

iron, barium and boron form carbides, which leads to the presence of carbon in the metal. Such a ferroalloy can be used for alloying and modifying cast iron. For a limited conversion of carbon to metal in order to alloy it, for example, steel, a method of orethermal smelting with a lack of carbon can be used. In the charge (3), all input parameters were retained, but the carbon consumption was reduced from 47,15 to 20 grams, i.e. more than 2 times. The processing results of a new (No. 4) charge are shown in Figure 3. It follows from this that in this case the ferroalloy is formed mainly from phases that do not contain carbon. So, at a temperature of 2 373 K characteristic inside the ore - thermal furnace, the alloy does not contain Fe_3C, B_4C, BaC_2, but contains only FeB and BaB_6 in the amount of 0,17 and 0,11 mass fractions, respectively. The unspent portion of the charge oxides forms a slag consisting of BaO and B_2O_3, represented by the phase BaB_2O_4. The presence of a strong base (BaO) at a low melting point [21] allows us to consider such a slag as a flux for secondary cleaning of metals from sulfur, arsenic, and phosphorus. Being a waste product, it will be cheaper than flux obtained from natural barite and borate ores, tested for these purposes . The compositions of the smelting products for all calculation options are presented in the Table 1 and Table 2.

Table 1 **Charge smelting products**

Nº	The composition of the melting products / g				
	Metal				Total
	Fe	Ba	B	C	
1	13,29	50,89	2,74	9,66	76,58
2	13,26	53,08	2,14	10,07	78,54
3	11,87	18,92	11,83	0,2	42,82
4	14,15	7,64	6,34	-	28,13

They are given in mass units (grams). This allows to evaluate the output of the metal from the charge, the amount of slag formed, gas. Analysis of the obtained data allows us to conclude that the mixture 1 and 2 provide a high metal yield without the formation of slag. In metallurgy, such a process is known as slag-free. The resulting metal contains an increased amount of carbon, and it can be used to alloy and modify cast iron.

Metal from charge 3 has a low carbon content and can be used to improve the quality of steel. Melting a charge (No. 4) with a lack of carbon leads to a very low metal yield, which can negatively affect the process economy. Such a ferroalloy can only be recommended for smelting particularly low-carbon steel grades.

Table 2 **Charge smelting products**

Nº	The composition of the melting products / g									Total	Total
	Slag		Total	Gas							
	BaO	B_2O_3		CO	Ba	Ar	Fe	BO	B_2O_2		
1	-	-	-	21,31	1,31	0,67	0,13	-	-	23,42	100
2	-	-	-	19,38	1,17	0,67	0,24	-	-	21,46	100
3	-	-	-	56,35	-	0,59	0,02	0,08	0,14	57,18	100
4	16,66	7,57	24,23	33,07	-	0,71	0,03	1,32	12,51	47,64	100

CONCLUSION

An analysis of the data obtained allows us to conclude that the production of boron barium ferroalloy is fundamentally possible. By changing the ratio of BaO to B_2O_3, it is possible to obtain a metal with a high (for alloying cast iron) or low (for alloying steel) carbon content. The process can be conducted without the formation of slag or with its minimum amount, which in metallurgy is called slag-free. In the case of slag formation, it mainly contains BaO and B_2O_3, which can be considered as a flux for extra-furnace removal of harmful impurities from metals. In production, overheating of the melting is not recommended, because in this case, losses of boron, barium and iron in the form of volatile sublimates are observed. The process can be implemented in standard ore-thermal furnaces using natural barite and borate ores.

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