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:B₂O₃ (3:1), barium carbide (BaC₂), iron boride (FeB), and barium hexaboride (BaB₆) 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 Ermakovskiy (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.
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 $\text{Ba}_3\text{B}_2\text{O}_6$. The first product of the carbon thermal process is iron carbide, produced by the reaction $3 \text{Fe} + \text{C} \rightarrow \text{Fe}_3\text{C}$ (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 $\text{Ba}_3\text{B}_2\text{O}_6$ remains unchanged to high temperatures (Figure 2, a). The $\text{BaO}$ and $\text{B}_2\text{O}_3$ contained in it do not react with carbon or $\text{Fe}_3\text{C}$ 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 $3 \text{Ba}_3\text{B}_2\text{O}_6 + 2 \text{Fe}_3\text{C} + 34 \text{C} \rightarrow 9 \text{BaC}_2 + 6 \text{FeB} + 18 \text{CO}$ (2). After the exhaustion of iron carbide, the reduction process is carried out due to carbon $\text{Ba}_3\text{B}_2\text{O}_6 + 6 \text{C} \rightarrow 2 \text{BaC}_2 + \text{BaB}_2\text{O}_4 + 18 \text{CO}$ (3). These two reactions contribute to a rapid increase in concentration $\text{BaC}_2$. The emersion of barium hexaboride refers to a temperature of 2 273 K in an amount of 0.004 mass fractions, when $\text{BaB}_2\text{O}_4$ metaborate is involved in the reaction: $3 \text{BaB}_2\text{O}_4 + 16 \text{C} \rightarrow \text{BaB}_6 + 2 \text{BaC}_2 + 12 \text{CO}$ (4). The maximum amounts of $\text{FeB}$ (0.16 mass fractions) and $\text{BaC}_2$ (0.6 mass fractions) are observed at 2 273 K, and $\text{BaB}_6$ (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 $\text{BaC}_2$ found by calculation are higher than those observed during the reduction of barium from free oxide by the reaction $\text{BaO} + 3 \text{C} \rightarrow \text{BaC}_2 + \text{CO}$ (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 $\text{BaC}_2$ already at 1 473 K in an amount of 0.18$\times 10^{-3}$ mass fractions. $\text{BaC}_2$ reaches its maximum value (0.85 mass fractions) at 1 823 K, and not at 2 273 K as during reduction from $\text{Ba}_3\text{B}_2\text{O}_6$. 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 $\text{Ba}_3\text{B}_2\text{O}_6$ due to their bound state. Barium reduction can be facilitated from a charge in the quasi-binary $\text{Ba}_3\text{B}_2\text{O}_6$ - $\text{BaO}$ system due to the presence of free barium oxide in it. An example of melting such a mixture (2) of 60.57 $\text{BaO}$, 6.88 $\text{B}_2\text{O}_3$, 13.44 Fe and 18.38 C is shown in the figure 2,b. Here $\text{BaC}_2$ emerges at 1 473 K, but already in an amount of 0.23$\times 10^{-3}$ mass fractions. At the temperature of 1 773 K, there is an intensive increase in the amount of $\text{BaC}_2$ (up to 0.16 mass fractions) and a decrease in $\text{BaO}$ to zero. Since then, $\text{Ba}_3\text{B}_2\text{O}_6$ is involved in the reduction process, providing a further increase in concentration of $\text{BaC}_2$. Its maximum amount (0.63 mass fractions) falls on 2 223 K. $\text{FeB}$ emerges at 2 023 K in an amount of 0.14$\times 10^{-3}$ mass fractions with a further increase in its concentration with increasing temperature (Figure 2,b).
Barium hexaboride is formed in small quantities due to the early consumption of barium and boron oxides on the formation of $\text{BaC}_2$ and $\text{FeB}$.

A similar approach can be used to facilitate the reduction of boron of the fusible mixture (3) in the quasi-binary system $\text{BaB}_4\text{O}_7 + \text{B}_2\text{O}_3$ (Figure 3).

The presence of free $\text{B}_2\text{O}_3$ and obtained as a result of conversion at low temperatures according to the scheme $\text{BaB}_4\text{O}_7 = \text{BaB}_2\text{O}_4 + \text{B}_2\text{O}_3$ (6) promotes the reaction $3 \text{B}_2\text{O}_3 + 2 \text{Fe}_3\text{C} + 7 \text{C} = 6 \text{FeB} + 9 \text{CO}$ (7). The temperature of the highest FeB content (0.14 mass fractions) is much lower (1 623 K) than when it was obtained from $\text{Ba}_3\text{B}_2\text{O}_6$ (2 273 K), which reflects the difference in $\text{B}_2\text{O}_3$ 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 $2 \text{B}_2\text{O}_3 + 7 \text{C} = \text{B}_4\text{C} + 6 \text{CO}$ (8). After $\text{B}_2\text{O}_3$ is used, barium metabolite is involved in the reaction $\text{BaB}_2\text{O}_4 + 3 \text{C} + \text{B}_4\text{C} = \text{BaB}_6 + 4 \text{CO}$ (9). A temperature of 2 223 K accounts for a sharp decrease in the amount of $\text{C}$, $\text{B}_4\text{C}$, $\text{BaB}_2\text{O}_4$ and the emersion of $\text{BaB}_6$ (Figure 3). With this charge, $\text{BaC}_2$ 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 $\text{Fe}_3\text{C}$, $\text{B}_4\text{C}$, $\text{BaC}_2$, but contains only $\text{FeB}$ and $\text{BaB}_6$ in the amount of 0,17 and 0,11 mass fractions, respectively. The unspent portion of the charge oxides forms a slag consisting of $\text{BaO}$ and $\text{B}_2\text{O}_3$, represented by the phase $\text{BaB}_6\text{O}_4$. 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

<table>
<thead>
<tr>
<th>№</th>
<th>The composition of the melting products / g</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
<td>$\text{Ba}$</td>
</tr>
<tr>
<td>1</td>
<td>13.29</td>
<td>50.89</td>
</tr>
<tr>
<td>2</td>
<td>13.26</td>
<td>53.08</td>
</tr>
<tr>
<td>3</td>
<td>11.87</td>
<td>18.92</td>
</tr>
<tr>
<td>4</td>
<td>14.15</td>
<td>7.64</td>
</tr>
</tbody>
</table>

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.
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 B₂O₃, 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 B₂O₃, 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.

LITERATURE


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