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PRODUCTION OF BORBARIUM FERROALLOY

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In the present work, it was considered expedient to organize the production of binary borbaric ferroalloy. The simultaneous presence in it of barium and boron, known as an effective micro-alloying element, should provide it with a high demand for industry. The possibility of producing such a ferroalloy is based on the fact that boron according to the table of Mendeleev discovered a diagonal analogy with silicon and must, with barium, give a compound soluble in iron. To discover this, it was constructed a diagram of the phase composition of the Fe - Ba - B - C system, created its mathematical model and it was given the characteristics of the compounds formed in it. According to the data obtained, it was concluded that the possibility of implementing the technology is based on the formation of BaB_6 hexaboride, which is soluble in iron, between the barium and boron. It was estimated the size of the field of its crystallization and the features of coexistence with other phases of the metal. The possible binary compounds of borbaric ferroalloy are BaB_6, FeB, Fe_3C, B_4C and BaC_2. Melting of ferroalloy is offered by usual carbothermic method.

Key words: ferroalloy, boron, barium, phase composition, mathematical model.

INTRODUCTION

Modification and microalloying are effective means of improving the performance characteristics of ferrous and non-ferrous metals. As a modifier, barium was widely used. It has a low solubility in iron (0,003 %) and to overcome this threshold it is produced in the form of alloys with silicon or aluminum [1, 5]. In the first case, silicides (BaSi, BaSi2) that are well soluble in iron are formed, and therefore such alloys are called silicobarium or ferrosilicon with barium. But the volume of silicobarium production is much inferior to that of traditional ferroalloys.

In the present work, it was considered expedient to organize the production of borbaric ferroalloy. The simultaneous presence in it of barium and boron, known as an effective micro-alloying element [6, 7], should provide it with a high demand for industry.

WAYS OF STUDY

The possibility of producing such a ferroalloy is based on the fact that boron according to the table of Mendeleev discovered a diagonal analogy with silicon and must, with barium, give a compound soluble in iron.

To implement the process, it was planned to use a widespread carbothermal melting method, when boron and barium are reduced from oxides by carbon and give soluble in iron compounds. To do this it was identified a search for these compounds and, in order to preliminary assess the charac-teristics of the new ferroalloy, plotting the phase diagram of the system Fe - Ba - B - C.

To construct the diagram, it was used a method based on the thermodynamic estimation of the possibility of secondary compounds formation from the initial elements, as well as the principles of geometry and topology of diagrams [8, 9]. The phase composition diagram has a special and unlike view of state diagram. It is a diagram of coexisting phases. The latter are connected by straight lines. In this case, the diagram of a three-component system is a set of elementary triangles of coexisting phases, 4 - component - tetrahedra, 5 -pentatopes, etc. In the graphic representation, the diagram of the 4 -component system under study is a tetrahedron composed of one-component, binary and three-component systems, the list of which is given in Table 1.

Table 1 **List and number of partial systems**

Number		Systems
Comp	systems	
1	4	Fe; C; Ba; B
2	6	Fe - C; Fe - Ba; Fe - B; C - Ba; C - B; Ba - B
3	4	Fe - C - Ba; Fe - C - B; Fe - Ba - B; C - Ba - B
4	1	Fe - C - Ba - B

The construction of the phase composition diagram began with the partial three-component diagrams (Table 1), revealing binary and triple phases in their reference data. To construct the diagram, stable (congruently melting) compounds were used.

System Fe - C - Ba. There are three binary partial systems: Fe - C; Fe - Ba and Ba - C. In the first one it is formed congruently melting iron carbide (Fe_3C) [10]. In

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Table 2 **Coordinates and melting points of phases**

№	Compounds	Coordinates / wt. %				Melting temperature / K
	Formula	Fe	C	Ba	B	
1	Fe	100	0	0	0	1 811
2	C	0	100	0	0	3 820
3	Ba	0	0	100	0	1 000
4	B	0	0	0	100	2 348
5	FeB	83,78	0	0	16,22	1 923
6	Fe_3C	93,32	6,68	0	0	1 500
7	BaC_2	0	14,88	85,12	0	1 627
8	BaB_6	0	0	67,92	32,08	2 540
9	B_4C	0	21,72	0	78,28	2 623

the second system (Fe-Ba) there are no connections. According to [10], iron and barium do not form compounds in either liquid or solid state. In the Ba - C system, there is a presence of carbide BaC_2.

Triangulation using the method [8, 9] leads to the breakdown of the Fe - C - Ba system into three triangles of coexisting phases: 1.Fe_3C - C - BaC_2; 2. Fe_3C - BaC_2 -Fe; 3. Fe - BaC_2 - Ba.

System Fe - C - B consists of three binary systems: Fe - C; Fe - B и C - B. The first of these was discussed above. In the second, there are two iron borides - one stable (FeB) and one decaying (Fe_2B) [10]. In the third system (C - B) there are two boron carbides, one of them melts with decomposition ($B_{13}C_2$), another one congruently (B_4C) [11]. Congruent connections are used for construction. Triangulation leads to the formation of 4 triangles of coexisting phases: 1.Fe - FeB - Fe_3C; 2. FeB - Fe_3C - C; 3. FeB - C - B_4C; 4. FeB - B_4C - B.

System Fe - Ba - B is formed by three binary systems :1.Fe - Ba, 2.Fe - B and 3.Ba - B**.** The first two systems were considered above. A search has shown [12] that BaB_6 hexaboride characteristic for all alkaline earth elements is formed in the Ba - B system, which can be the basis for obtaining a new ferroalloy. With triangulation, the particular Fe - Ba - B system is split into 3 triangles of coexisting phases: 1.Fe - FeB - Ba; 2. FeB - Ba - BaB_6; 3. FeB - BaB_6 - B.

System Ba - C - B consists of three binary systems: 1.C - Ba, 2.C - B and 3.Ba - B. All of them were considered above. According to the triangulation, the C - Ba - B system is divided into 4 triangles of coexisting phases: 1.Ba - BaC_2 - BaB_6; 2. BaB_6 - BaC_2 - C; 3. BaB_6 - C - B_4C; 4. BaC_2 - B_4C - C. Table 2 shows the characteristics of all phases.

RESULTS AND DISCUSSION

The presence of phase diagrams of particular three-component systems allows, using the usual methods [8, 9], to break up into elementary tetrahedrons a four-component system Fe - C - Ba - B. They were 7: 1. Fe - Ba - BaC_2 - FeB, 2. Fe - BaC_2 - Fe_3C - FeB, 3. Fe_3C - BaC_2 - C - FeB, 4. FeB - C - B_4C - BaB_6, 5. FeB - B_4C - B - BaB_6, 6. Ba - BaB_6 - BaC_2 - FeB, 7. FeB - BaB_6 - C - BaC_2 (Figure 1).

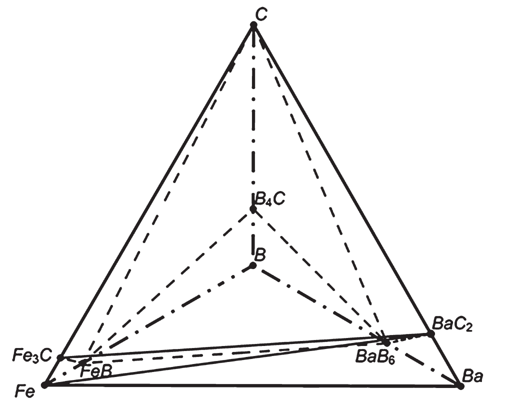

Figure 1 Phase composition diagram of the system Fe-Ba-B-C

It can be seen that there are 9 stable phases in the system under study. Four of them are one component: Fe, Si, Ba, B and 5 binary: FeB, Fe_3C, B_4C, BaC_2 and BaB_6. The determination of the phase composition by geometric constructions in a tetrahedron is possible, but difficult. Geometric method is generally not applicable for 5 or more component systems, because on the plane they can not be correctly displayed. For this reason, using the method developed by us [13], it was created a mathematical model of the diagram. It is compiled for each elementary tetrahedron and it is a system of linear equations connecting the chemical composition of the parent metal with its phase. For example, for tetrahedron №1 Fe - Ba - BaC_2 - FeB they are : $Fe = Fe_0 - 5,165 \cdot B_0$, $Ba = Ba_0 - 5,72 \cdot C_0$, $BaC_2 = 6,72 \cdot C_0$ and $FeB = 6,165 \cdot B_0$, where Fe, Ba, BaC_2, FeB are determined phases and Fe_0, Ba_0, C_0 and B_0 is the content of iron, barium, carbon and boron in the metal by chemical analysis. The simplicity of the algorithm made it possible to create a computer program, which greatly accelerates the calculations. In the case of the task of the chemical composition panel of the metal, the computer inserts it into all tetrahedra and finishes the calculation when 100 % of the sum of all phases in a tetrahedron is received, denoting the number of this found tetrahedron. The phase composition is given in percent by weight.

The coordinates of the vertices were found by the volume of each tetrahedron. This made it possible to estimate the volume of crystallization fields of each phase of the system Fe - C - Ba - B. This is important for

Table 3 **The volumes of tetrahedra and the probability of phases existence (W_i)**

№	Phases	Amount of tetrahedrons which are in the phase	The total volume of tetrahedra, which includes the phase (∑V)	Probability of phase existence (W_i)
1	Fe	2	0,0333	0,008325
2	C	2	0,6871	0,171775
3	Ba	2	0,0641	0,016025
4	B	2	0,2396	0,059900
5	Fe_3C	2	0,138	0,034500
6	FeB	7	1	0,250000
7	BaC_2	7	1	0,250000
8	BaB_6	2	0,1247	0,031175
9	B_4C	2	0,7132	0,178300

the smelting of the metal of a given composition. Such information is given in the table 3. It can be seen that the phases can participate in the construction of several tetrahedra, for example, Fe - two, and FeB - seven, occupying the corresponding volumes (∑V). If the last value is divided by the sum of such volumes, then the prevalence of this phase in the tetrahedron can be obtained. It is called the probability of existence of a phase (W_i) [8]. It can be seen from the table that prevalence in the phase space is dominated by BaC_2 and FeB.

Smelting in large fields increases the stability of the operation of the ore-thermal furnace both in terms of productivity and the production of a stable metal. The appearance in the metal of the binary phases listed in Table 3 is expected from the reactions:

$BaO + 3B_2O_3 + 10C = BaB_6 + 10CO$, $BaO + 3C = BaC_2 + CO$, $2B_2O_3 + 7C = B_4C + 6CO$, $3/2B_2O_3 + Fe_3O_4 + 17/2C = 3FeB + 17/2\ CO$ and $Fe_3O_4 + 5C = Fe_3C + 4\ CO$.

In conditions of real melting, in addition to those mentioned above, other reactions that can change the process can also occur. In this case, complete thermodynamic analysis of the process being developed using specially developed complexes [14-19]. In order to correctly carry it out, the necessary data for thermodynamic modeling have been additionally introduced into the database of the TERRA complex [20] used.

CONCLUSION

Thus, theoretical studies show the possibility of creating a borbaric ferroalloy by the usual carbothermic method. Simultaneous presence of a strong alloying and modifying element makes it possible to consider it as an effective means of improving the quality of ferrous and non-ferrous metals.

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