Production of Ferroboron from Wastes by SHS-metallurgy and influence of Ligatures on the Structure/Properties of Cast Iron

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Abstract. Waste, generated during the industrial process negatively affects the environment, but at the same time it is a valuable raw material and can be used to produce new marketable products. The study of the effectiveness of Self-propagating High temperature Synthesis (SHS) methods, which are characterized by the simplicity of the necessary equipment, the purity of the final product and the high processing speed, is under the wide scientific and practical interest to solve the set problem. The work describes technological aspects of production of ferro boron by the method of SHS - metallurgy from iron-containing wastes of rolled production for alloying of cast iron and results of effect of alloying element on degree of boron assimilation with liquid cast iron. Features of Fe-B system combustion have been investigated and the main parameters to control the phase composition of synthesis products have been experimentally established. Effect of overloads on patterns of cast ligatures formation and mechanisms of structure formation of SHS products was studied. It has been shown that an increase in the content of hematite Fe₂O₃ in iron-containing waste leads to an increase in the content of phase FeB and accordingly, the amount of boron in the ligature. Boron content in ligature is within 3-14%, and phase composition of obtained ligatures consists of Fe₂B and FeB phases. Depending on the initial composition of the wastes, the yield of the end product reaches 91 - 94%, and the extraction of boron is 70 - 88%. Combustion processes of high exothermic mixtures allow obtaining a wide range of boron-containing ligatures from industrial wastes. In view of the relatively low melting point of the obtained SHS-ligature, the positive dynamics of boron absorption by liquid iron is established. According to the obtained data, the degree of absorption of the ligature by alloying gray cast iron at 1450 °C is 80 - 85%. When combined with the treatment of liquid cast iron with magnesium, followed by alloying with the developed ligature, boron losses are reduced by 5 - 7%. At that uniform distribution of boron micro-additives in volume of treated liquid metal is provided.

1. Introduction
Due to the growth in industrial production under the influence of scientific and technological progress, an acute problem arises in connection with environmental pollution. Waste from industrial activities is increasingly polluting the human environment, while the main source of pollution is the return to nature of the mass of waste that is generated in the production process. At the same time, the waste generated at the enterprises is a valuable raw material and can be used to obtain marketable products...
The processing of iron-containing mill scale is very problematic and difficult, especially the fine fraction <100 μm. In industry, scale is agglomerated or briquetted and then introduced to adjust the composition of the steel. This requires a lot of energy, and when melting steel, the fine fraction is emitted in the form of dust and gases, or passes into slag, which also has a negative impact on the environment. Therefore, obtaining a valuable product from iron-containing fine-dispersed waste is an important and urgent task. This problem can be solved by environmentally friendly, low waste progressive SHS - metallurgy (Self-propagating High-temperature Synthesis) [3-6]. The technology allows using a finely dispersed fraction of industrial waste with minimal energy consumption to obtain valuable products from them. The main advantages of SHS - processes are the simplicity of the equipment, the purity of the final product, the speed of the process, the ecological purity of the SHS process, etc. A feature of the SHS technology is that there is practically no gas evolution during the process and completely condensed products are formed. Very high temperatures (up to 4000 °C) can be developed in the condensed phase. However, the duration of this high temperature is very short, determined by the speed of propagation of the combustion front and the amount of exothermic mixture. High temperatures in the condensed phase (liquid - viscous state), high heat capacities of combustion products, low values of mass transfer constants, peculiar kinetic laws of chemical interaction, high-temperature phase transitions, all characterize a specific picture of the SHS process. In addition, in these processes, a waste-free chemical synthesis of the resulting compounds occurs [7-8]. The purpose of this work was to obtain valuable products from industrial waste by effective SHS-metallurgy and to study the effect of the alloying element on the degree of boron assimilation by liquid iron. The SHS process is based on the use of thermodynamic calculations of SHS systems, which are based on the calculation of the adiabatic combustion temperature to determine the fundamental possibility of combustion reactions. This makes it possible not only to determine the fundamental possibility of obtaining materials of the selected composition in the SHS mode, but also to predict some conditions for preparing and carrying out the synthesis, thereby without resorting to long-term experimentation.

2. Experimental Procedures
The studies were carried out using a laboratory SHS - centrifugal machine, with the rotation speed from 1000 to 2500 rpm. The synthesis of the final products was carried out in graphite reaction vessels with an internal diameter of D = 40 mm and a height of H=100 mm. The experimental technique is standard [9]. The products obtained were investigated by X-ray phase, chemical, metallographic and micro spectral analysis. To obtain the final products, a boron-containing material in the form of B₂O₃, iron-containing wastes of rolling production, slag thinners were used, and aluminum powder was used as a reducing metal.

In the experiments, the influence of technological parameters (such as phase separation, scatter of the reaction mass, composition and dispersion of components, density of the initial mixture) on the regularities of the synthesis of cast ligatures in the Fe-B system was studied. The influence of overloads on the regularities of the synthesis of cast master alloys and the mechanisms of structure formation of SHS products have been studied.

Three different types of waste, conventionally designated by the symbols S1, S2, and S3, were used as an iron-containing component of the exothermic mixture, which differed in the ratio of magnetite (Fe₃O₄), hematite (Fe₂O₃) and FeO, as well as in the amount of various impurities (Figure 1).
3. Results and Discussions

The phase composition of the ligatures obtained from various types of iron-containing waste (scale), consists mainly of the Fe$_2$B and FeB phases, while the yield with the use of waste:

- S1 is 91% and boron recovery is 70%. The final product contains phases $\sim$ 65% FeB, and phases Fe$_2$B $\sim$ 35%;
- S2 is 94% and boron recovery 77%. The final product contains $\sim$ 65% Fe$_2$B phase, and FeB phase $\sim$ 35%;
- S3 is 95% and boron recovery is 88%. The final product contains $\sim$ 85% Fe$_2$B phases and $\sim$ 15% FeB phases.

Figure 2 shows the effect of engine speed, i.e. centrifugal force to the depth of dispersion of the reaction mixture h1, for compositions of pure oxides of FeO and hematite Fe$_2$O$_3$.

Figure 1. Chemical composition of iron-containing R1, R2 and R3 wastes

Figure 2. The influence of centrifugal force on the depth of spread h1, depending on the type of iron-containing product used: 1 - S1; 2 - S2 and 3 - S3.
It was found that with an increase in the centrifugal force for compositions using hematite, emissions decrease linearly, and for compositions using FeO, emissions decrease slightly and reach saturation at 2000 rpm.

Figure 3 shows the effect of engine speed, i.e. centrifugal force on the yield of the target product (h2), for compositions of pure oxides of FeO and hematite Fe₂O₃.

![Figure 3](image)

**Figure 3.** Influence of centrifugal force on the completeness of the target product yield (h2), depending on the type of iron-containing product used: 1 - S1; 2 - S2 and 3- S3.

It was found that with an increase in the centrifugal force for compositions using hematite and FeO, the yield of the alloy passes through a maximum at 2000 rpm.

In addition, the increased scatter of the initial components for composition 1 (Figure 2) is associated with the presence of an excess amount of an energy additive (NaNO₃) in the charge, which logically affected the alloy yield (Figure 3). According to the preliminary experiments carried out under centrifugal force, the results of X-ray phase analysis (on the DRON-2 and DRON-4 devices) showed that when obtaining a ferroboron master alloy from FeO, the final product consists of Fe₂B and FeB phases in which the Fe₂B phase prevails. At the same time, the preparation of a master alloy from hematite Fe₂O₃ in the presence of the same phases is dominated by the FeB phase. In the case of using industrial waste from magnetite Fe₃O₄, the quantitative content of the Fe₂B and FeB phases depends on the initial content of FeO and hematite in the waste (Figure 1).

This can be explained by the following reasoning. Based on them below the parameters of the adiabatic combustion temperature and the heat effect of the reaction in the oxidative - reduction reaction of Fe₃O₄, FeO and Fe₂O₃ with aluminum are given below:

\[
3/4 \text{Fe}_3\text{O}_4 + 2\text{Al} \rightarrow 9/4 \text{Fe} + \text{Al}_2\text{O}_3 \quad \Delta H = 838 \text{ kJ/mol; } t_{\text{ad mountains.}} = 3200 \text{ °C} \\
3\text{FeO} + 2\text{Al} \rightarrow 3\text{Fe} + \text{Al}_2\text{O}_3 \quad \Delta H = 880 \text{ kJ/mol; } t_{\text{ad mountains.}} = 3194 \text{ °C} \\
\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 \quad \Delta H = 860 \text{ kJ/mol; } t_{\text{ad mountains.}} = 3428 \text{ °C} 
\]

It can be concluded that the reaction of FeO with Al does not have enough temperature for the formation of a large amount of FeB, which practically corresponds to the thermodynamic calculation. For the case of Fe₂O₃ and Al, the combustion temperature is high enough for the formation of the FeB phase, also confirmed by thermodynamic calculations. In our case, when we use waste in the form of magnetite with different contents of FeO and hematite, we obtain a mixture of phases from Fe₂B and FeB, and the more iron oxides in the waste in the form of hematite Fe₂O₃, the greater the content of...
FeB and thus the amount of boron in the master alloy. The studies carried out on the MAGELLAN Q8 device have established that carbon for all investigated materials ranges from 0.01 - 0.2%. It has been established that the content of carbon and other iron-containing components involved in the synthesis of materials depends on the type of pure iron oxides, as well as the origin and places of scale formation during rolling steel production technology. Thus, the ferroboron master alloy obtained from S2 waste contains boron in an amount of not more than 10%, and from S3 it contains boron in an amount of not less than 14%. Alloaying of grey cast iron for simplicity of calculations was carried out with SHS-ferroboron alloy with a boron content of 10%, i.e. obtained from S2 waste. Smelting of cast iron in an amount of 10 kg was carried out in an induction furnace with a capacity of 50 kg. The cast iron was overheated (for complete dissolution) to a temperature of 1450°C, into which 60 gr of SHS of ferroboron alloy was introduced, so that boron in alloyed cast iron would be at least 0.06%. After making samples for chemical and metallographic analyses, it was found that:

- the average boron content before alloying was 0.0008 wt%, and after alloying 0.066 wt%;
- in the original grey cast iron, the average hardness (HRA) was 43.2 units, and after alloying 57.2 units;

Thus, the alloying element was very well dissolved in grey cast iron, changed its chemical composition and increased its hardness by 20 units, and also changed its structure.

In figure 4a shows the structure of the initial gray cast iron etched (1% solution of nitric acid), taken on the device "NEOFOT 21". It can be seen that the structure consists of a ratio of ~ 60% (dark areas) of pearlite and 40% (light areas) of ferrite.

![Figure 4a](image)

**Figure 4a.** Etched grey cast iron a - before alloying and b - after alloying

Figure 4b shows an etched sample doped with ~ 10% boron in ferroboron. A dispersed structure is also visible here, it also consists of pearlite and ferrite, but already with a ratio of ~ 80/20. In this case, ferrite is already located along the grain boundaries of perlite. Investigations of the structures also showed that the structure with lamellar graphite sharply decreased (Figure 4a) and after alloying (Figure 4b) in places the graphite shape became flaky.

In order to study the feasibility of using the developed ferroalloys in the production of high-strength cast iron, various combinations of the processes of spheroidizing modification and micro allying of the cast iron melt have been investigated. Therefore, to study the feasibility of using the developed ferroalloys in the production of high-strength cast irons, various combinations of processes of spheroidizing modification and micro alloying of cast iron melt were investigated. In particular, according to the first variant, the cast iron melt was first micro alloyed with ferroboron, and then it was modified. According to the second variant, the already pre-modified cast iron was micro alloyed. For microalloying the melt, both developed (10% B) and industrial ferroboron with 17% boron were used, and metallic magnesium was used as a modifier, which was fed into the lower layers of the molten metal using a graphite bell. To assess the effectiveness of the presented technological schemes for melting
alloys, the chemical composition, mechanical and structural characteristics of high-strength cast irons were recorded. The addition of ferroalloys was carried out based on the introduction of 0.03% boron into the cast iron melt. As you know, the optimal temperature for inoculating cast iron with magnesium vapor from the point of view of the thermodynamics of the process is 1320-1330 °C. The comparison of the main characteristics (melting point, density, melting time) of the selected ferroalloys and the peculiarities of their interaction with the processed melt is carried out. Boron microadditives were introduced at various temperatures of liquid iron - from 1430 to 1480 °C. According to the data obtained, the use of the SHS ligature in the specified temperature range provides a more complete assimilation of the alloying element by the melt, which reaches its limiting values at 1450-1460 °C (Figure 5). At the same time, the content of boron in cast iron from the moment of the end of microalloying of liquid metal to the end of its casting into molds remains stable and amounts to 0.028 ... 0.031%.

![Figure 5](image_url)

**Figure 5.** Influence of the processing temperature of liquid iron on the degree of assimilation of boron
1. modification of cast iron with Mg -> microalloying with SHS - with ferroboron
2. microalloying with SHS - ferroboron -> modifying cast iron with Mg
3. microalloying with ferroboron FB 0 (17% B) -> modification of cast iron with Mg

The rapid dissolution of the SHS master alloy, high assimilation and uniform distribution of boron in the volume of the cast iron melt is explained by the fact that the SHS technology makes it possible to increase (~1.15 times) the density of the boron content in the developed ferroalloy and reduce the melting temperature of the developed alloy by reducing the content in it boron up to 10%. The density of ferroboron with 17% boron is 5.6 - 5.8 g / cm3, and SHS - ferroboron with 10% boron is 6.4 - 6.5 g / cm3. Regardless of the deoxidation option, the prototypes of ductile iron are characterized by a low level of contamination with non-metallic inclusions.

It has been experimentally established that the effectiveness of the use of SHS master alloy can be improved (increased) if the cast iron melt is preliminarily subjected to treatment with a magnesium modifier before alloying. The magnesium introduced in this case causes spheroidization of graphite inclusions and binds oxygen and nitrogen dissolved in the metal into strong chemical compounds Mg₃N₂ and MgO, as a result of which their interaction with boron is prevented.

The high thermodynamic activity of magnesium provides a decrease (decrease) in the content of oxygen in cast iron by 80-87% and nitrogen by 24 - 27% (table 1) and, as a consequence, reduction (reduction) of boron losses during alloying by 5 ... 7%. Thus, microalloying the melt with boron at the final stages of the processing of liquid iron is technologically more justified, since it improves the utilization rate of the ferroalloy.
Table 1. Effect of magnesium on the gas content in cast iron before and after modification

| Liquid metal processing mode                                      | Gas content in cast iron before and after modification,% | Boron assimilation,% |
|------------------------------------------------------------------|----------------------------------------------------------|----------------------|
|                                                                  | oxygen | Nitrogen |                                      |
|                                                                  | before | after    | before | after |
| Alloving SHS with ferroboron at 1460 °C + modification at 1330 °C | 0,0070 | 0,0035   | 0,0040 | 0,0018 | 81     |
| Modification of SHS with ferroboron at 1460 °C + alloying at 1330 °C | 0,0072 | 0,0011   | 0,0038 | 0,0021 | 87     |

The content of gases was determined on installations manufactured by the company "Balzers" and an analyzer TS-500 LECO.

Metallographic analysis of the investigated high-strength cast irons shows that under the influence of boron microadditions in the metal matrix, dispersed inclusions of nitrides, boron carbonitrides (<2 μR) and iron borides are formed, which are located along the grain boundaries and increase the mechanical and operational characteristics in general.

An increase in the fineness of the structure, the formation of new phase boundaries, an increase in the diffusion activity of carbon, and the refinement of graphite inclusions provide the formation of bainite structures during isothermal quenching without alloying high-strength cast irons with expensive and scarce Mo, Ni, and Cu (Figure 6) [10].

![Figure 6](image_url)

**Figure 6.** Microstructure of boron microalloyed ductile irons- X 1000
- a - isothermally hardened at 400 °C; b - isothermally hardened at 300 °C;

Thus, the technological features of microalloying high-strength cast irons have been studied and the main parameters have been established for the effective action of the developed SHS master alloy on the liquid metal. The advantages of the developed SHS ferroboron in comparison with the currently most used ferroboron grades FB0 (≥20% V) and FB1 (≥17% V) are shown. The data obtained substantiate the feasibility of obtaining ferroalloys by SHS technologies that allow the use of cheap and unconventional raw materials.

4. Conclusions

1. The paper presents technological aspects of production of ferroboron by method of SHS - metallurgy from iron-containing wastes of rolling production for alloying of cast iron. Features of Fe-B system combustion have been investigated and the main parameters of control of phase composition of synthesis products have been experimentally established.
Effect of overloads on laws of synthesis of cast ligatures and mechanisms of structure formation of SHS products was studied.

2. It has been found that with an increase in the content of hematite in iron-containing waste, it contributes to an increase in boron recovery, which reaches 88%.

3. It has been found that the produced 10% boron ferroborron SHS has a high absorption and uniform boron distribution throughout the casting volume, and allows it to be effectively used in iron alloying.

4. Developed technology of production of ferroboron by SHS-metallurgy allows to use hard-to-process finely dispersed iron-containing wastes of rolling production, to obtain cheap and valuable product from them, and at the same time to improve the ecological situation of the region littered with waste production.

Experiments have shown that an increase in the content of hematite Fe$_2$O$_3$ in the iron-containing waste and thereby a decrease in the content of FeO leads to an increase in the content of the FeB phase and a decrease in the Fe$_2$B phase in the target product.

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