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# Prospects for Using Boron in Metallurgy. Report 2

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**Abstract**—The second part of the article presents perspective directions of using boron and its compounds in the preparation processes, metallurgical processing of ore materials and steel smelting in order to improve the quality of the final product. An efficient technology of silicothermal production of ferrosilicoboron containing 0.6–2.0% B and 60–80% Si has been developed. The advantage of this scheme is the possibility of obtaining a boron-containing alloy during ferrosilicon smelting. It has been experimentally shown that ferrosilicoboron has higher performance characteristics than ferroboron both in production and when used for steel processing. The industrial test results of the technology for microalloying pipe grades of steel with a new ferroalloy with boron confirmed a high degree of boron assimilation—up to 96%. The possibility of widespread use of boron for steel microalloying is due to its cheapness, availability and environmental friendliness. According to the calculations, boron from complex ferrosilicoboron is the cheapest trace element used to increase the strength characteristics of steel. Additives of $B_2O_3$ can be successfully used to form high-magnesium liquid steel-making slags. It is shown that 0.37–0.55% $B_2O_3$ effectively stabilizes the highly basic slags of the steel and ferroalloy industries. This operation allows obtaining a marketable lump material. The above review as well as the results of the laboratory and industrial studies have shown the effectiveness of boron usage at different stages of metallurgical production. An increase in technical and economic indicators of production and quality of steel and ferroalloys, as well as effective disposal of waste slags, is shown. The technical solutions advanced and tested at metallurgical enterprises do not require capital expenditures. They are implemented by adding microdosing of boron and its compounds to metallurgical production facilities.

**Keywords:** metallurgy, boron, ferroalloy, steel, slag, physical and chemical characteristics, microalloying, stabilization

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## INTRODUCTION

Currently, conditions of production boron is introduced into metal melt in the form of ferroalloys. In Russia and abroad, mainly ferroboron containing 6–24% B is applied [1, 2].

Besides ferroboron, complex boron-containing ferroalloys are applied for alloying steel and cast iron with boron. The use of these alloys increases the efficiency of alloying of steels with boron as compared with ferroboron [3].

The composition of complex alloys includes technologically necessary elements, which amplify the effect of microalloying with boron (Si, Al, Ti, Ca). In Russia and abroad, these alloys are produced in a large assortment.

Boron-containing ferroalloys are produced by carbo-, alumino- and silicothermal method of reduction of boron from oxides as well as remelting of metal of various composition.

Reduction of boron by carbon to carbide $B_4C$ is thermodynamically more preferable. Since boron carbide is a very strong chemical compound, then the alloys obtained during carbothermy will contain up to 2% C.

Combined reduction of boron and silicon by oxygen from oxides allows obtaining alloys with low content of carbon. The processes of carbothermal obtaining of boron-containing complex ferroalloys during combined reduction of boron, silicone, manganese and nickel are widely spread.

The aluminothermal method of obtaining alloys with boron became widespread due to high reductive ability of aluminum. This method is used to obtain the most widespread ferroalloy in the world—ferroboron.

Boron anhydrite (95% $B_2O_3$) or boric acid (52–55% $B_2O_3$) are used as the main material during smelting of ferroboron with increased content of boron (grades FB20 and FB17). Ferroboron with decreased content of boron (6–10%) is obtained using borate ore (8–20% $B_2O_3$; 1.5–10% $SiO_2$; 15–25% CaO; 10–30% MgO; 3–5% FeO). Borate ore contains large amount of crystal water, carbon and sulfur. In order to remove harmful impurities, borate ore must be subjected to firing in a pipe furnace at 700–800°C.

As a rule, powder of primary aluminum is used as a reducing agent for aluminothermal production of ferroboron of grades FB20 and FB17, ferroboron of other grades is reduced using secondary aluminum shavings. Iron is introduced into the composition of the charge in the form of a low-phosphorous iron ore or rolling iron scale. The main flux addition in the charge for obtaining ferroboron is represented by freshly burned lime.

Disadvantages of ferroboron are concluded in the application of expensive charge materials (aluminum, boron anhydrite) when obtained, as well as low degree and stability of boron assimilation during microalloying of steel.

Wide application of boron for microalloying of steel is conditioned by its cheapness and availability, application safety and environmental compatibility.

In metallurgy, boron is used for modifying and microalloying of [4–10]:

— cast irons of all the basic classes (malleable, grey, modified, white) in order to impact the formation of cast structure and regulate graphitization;

— structural low-alloyed and high-strength steels for increasing hardening capacity and mechanical characteristics;

— heatproof steels and steels based on iron, chromium and nickel for increasing mechanical characteristics and heat-proof properties at increased temperatures;

— corrosion-resistant steels and alloys based on iron, chromium and nickel to increase resistance against intercrystalline corrosion (ICC) in weakly oxidizing media and corrosion cracking;

— stainless steels of various structural classes used in atomic power engineering, including production of elements of biological shielding;

— cast hard-melting alloys based on molybdenum and tungsten for refining the structure and purification of metal from oxygen and increasing of its plasticity;

— amorphous boron-containing alloys.

Microalloying of steel with boron provides increasing of resistance of the austenite to decay during its subcooling [11] and as a result, increasing of the efficiency of hardening capacity. As known, microalloying of a low-carbon steel with boron doubles the depth of the hardened layer.

If manganese, chromium and molybdenum improve the hardening capacity when introduced in increased amounts, then the positive impact of boron appears at its very small concentrations. The optimal amount of boron, causing the largest increment of the hardening capacity of structural steel, is determined by its composition and, according to some authors, caries within the limits of 0.0005–0.0100%.

The efficiency of introduction of boron decreases with growth of austenitization temperature. In contrast to boron, such alloying elements as manganese, chromium and molybdenum improve the hardening capacity with growth of preheating temperature for hardening.

Boron can influence the properties of steel as follows [12–16]:

— to increase the plasticity;

— to reduce the negative effect of free nitrogen by binding it into carboboronitride compounds, which increases the plasticity and deformability of rolling during cold deformation;

— to improve deformability of nonmetallic inclusions.

According to the author of work [17], microalloying with boron is one of the promising directions of increasing the operational and mechanical characteristics, saving unavailable alloying elements. Due to its high hardenability, strength and ductility in rolled and normalized state, as well as good weldability, boron is widely used in the production of low-alloy steel. Boron has low deoxidizing capacity, but forms stable nitrides. The optimal content of boron in steel constitutes 0.001–0.005%. At higher content (0.005–0.008%) it forms a low-melting eutectic, which is located along the grain boundaries, which reduced the strength properties of steel during heating. Thus, the content of boron in steel is strictly regulated.

It was shown that complex alloying allows preventing transcrystallization and refine the microstructure in castings [1, 18–21]. Boron has a tendency to form nitrides. Therefore, the authors recommend using active elements during deoxidation and degassing for a higher efficiency of introduction of small boron additions, since hardening capacity also depends on so-called effective boron, i.e., boron in solution.

The use of boron in production of modern highly strong steels for main pipelines is of particular importance. This is connected with the fact that traditional ways of strengthening of pipe steels are practically exhausted today. Modern pipe steels differ by fine-grained structure, the main component of which is bainite. At the same time, it was established that the higher the strength class of pipe steel, the greater the concentration of bainite in its structure should be.

The prospects of using boron in Russia may increase in condition of obtaining stable research results of its assimilation and determination of the optimal concentrations in metal.

## RESULTS AND DISCUSSION

The efficiency of alloying with boron significantly increases during its combined introduction into steel with chemically active elements (Al, Si, Ti, Zr). The assignment of the active components of the ferroalloy mainly consists in binding oxygen and nitrogen contained in steel into strong compounds, preventing their interaction with boron. In addition, these components positively influence the steel structure.

Due to super low content of boron in steel, it is reasonable to use a boron-containing ferroalloy with content decreased to 0.6–3.0% B. This allows increasing the mass of the boron-containing alloy introduced into the steel, increasing the degree and stability of boron assimilation.

To satisfy the mentioned conditions, it is necessary to apply complex (multicomponent) boron-containing ferroalloys. Complex ferroalloys (CF) should be created in the most favorable combinations of components, which promote the required effective impact on iron-carbon melt and structure of hard metal at high degree of assimilation of useful components in it. It is worth noting that ore raw materials of lower quality as compared with smelting of standard alloys can be used to obtain complex ferroalloys. For example, non-conditional materials, production wastes, poor and complex ores and concentrates [22]. Due to low cost of non-traditional raw materials, the possibilities of its use and utilization the cost of CF will be lower and a new source of raw materials of ferroalloy production will appear [23, 24].

Ferroalloy production practice shows that due to more flexible regulation of technological parameters of the process CF smelting, such as the composition and temperature of slag melting, softening and electric resistance of the charge, it is possible to obtain alloys in melting units with higher technical-economical indicators. In addition, CF can be obtained by other methods, for example, suspension casting. This method is concluded in the introduction of a material of another composition, which being dissolved changes the composition of the initially cast metal, into liquid ferroalloy, located in the mold of a conveyor-type casting machine during casting.

Research has been carried out aimed at the development of a rational composition and effective technology for obtaining new complex ferroalloys with boron.

To determine the characteristics and rational composition of CF, a complex scheme has been developed and applied in IM UD RAS, which includes the following stages:

— preliminary adjustment of elements in the alloy in accordance with the composition and given properties of the processed metals;

— determination of the rational correlation of the elements based on studying physical-chemical properties of the alloys and the peculiarities of their interaction with the processed alloy [25].

Table 1 presents the compositions of the studied complex boron-containing ferroalloys and their basic physical-chemical characteristics: $t_b$—temperature of beginning of crystallization; ρ—density; $C_s$, $C_l$—specific heat capacity of solid and liquid alloys; $L$—melting heat; λ—heat conductivity; $\tau_\Sigma$—total melting time of ferroalloy; $\Sigma\Delta T$—total change of steel temperature during introduction of 1% of alloy into it [2].

Comparison of the characteristics of alloys of system Fe–Si–B and Fe–B shows that all silicate alloys have more favorable service characteristics: lower $t_b$ (1273–1480°C against 1430–1540°C), density, $\tau_\Sigma$ and $\Sigma\Delta T$.

When developing an effective technology of obtaining ferrosilicoboron, it was accounted that it is reasonable to obtain a highly silicate alloy using silicothermal method.

Physical-chemical computations and experimental melting on determination of the basic technological parameters of the process have been carried out. For ore-boron containing raw materials, it is reasonable to use Turkish colemanite, which contains, %: 37–40 $B_2O_3$; 25–30 CaO; 2–9 $SiO_2$; ~2 MgO. In hardened colemanite, the content of $B_2O_3$ reaches 47–49%.

Reduction of boron from colemanite by silicon of ferrosilicon (65 and 75% Si) was studied in laboratory conditions in a high-temperature electric furnace at temperatures of 1550–1650°C. With an increase in the reaction time of the reagents to 15–20 min, $K_B$ (the degree of transition of reduced boron to the alloy) increases by 25–30%, and the value of $K_B$ reach 65–70%. Assimilation of boron in the production of alloys with 1 and 2% B differs slightly.

An important link in the technology of obtaining a complex ferroalloy is the preparation of boron-containing raw materials. Boron-containing materials must ensure the production of ferrosilicoboron of the required composition. These may include, for example, fused or calcined colemanite in the form of powder or briquettes, or other similar materials, during processing which do not observe dust and gas emissions exceeding the existing standards.

Based on the conducted researches, an effective technology of silicothermal obtaining of ferrosilicoboron containing 0.6–2.0% B and 60–80% Si was developed. The method is concluded in reduction of boron from borate raw materials by silicon of ferrosilicon when introducing this raw material into the ladle during release of the alloy from the ore-reduction electric furnace [26].

Selection of this technology is conditioned by:

— the possibility of obtaining a boron-containing alloy along the way, when smelting ferrosilicon;

**Table 1.** Chemical composition and physicochemical characteristics of boron-containing ferroalloys

| No. | Alloy | Content*, % | | Characteristics of alloys | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | B | Si | $t_b$, °C | ρ, kg/m$^3$ | $C_s$, J/(kg deg) | $C_l$, J/(kg deg) | $L$, kJ/kg | λ, W/(m deg) | τΣ, s | Σ$\Delta T$ |
| 1 | FSB 25/1 | 1 | 25.0 | 1395 | 6200 | 486 | 770 | 328 | 25.7 | 91.2 | –19.5 |
| 2 | FSB 25/5 | 5 | 24.0 | 1418 | 6000 | 304 | 780 | 1092 | 24.7 | 101.1 | –27.0 |
| 3 | FSB 25/10 | 10 | 23.0 | 1443 | 5570 | 526 | 793 | 1249 | 23.5 | 115.2 | –43.4 |
| 4 | FSB 45/1 | 1 | 44.5 | 1275 | 5520 | 527 | 800 | 1253 | 25.7 | 86.8 | –18.8 |
| 5 | FSB 45/2 | 5 | 43.0 | 1350 | 5340 | 540 | 832 | 1354 | 24.7 | 91.1 | –24.0 |
| 6 | FSB 45/3 | 10 | 40.5 | 1400 | 5160 | 568 | 869 | 1456 | 23.5 | 102.1 | –35.0 |
| 7 | FSB 75/1 | 1 | 74.0 | 1258 | 3820 | 608 | 846 | 1600 | 25.7 | 72.8 | –6.8 |
| 8 | FSB 75/5 | 5 | 71.0 | 1273 | 3530 | 611 | 862 | 1650 | 24.7 | 68.6 | –16.6 |
| 9 | FSB 75/10 | 10 | 68.0 | 1358 | 3390 | 619 | 880 | 1700 | 23.5 | 71.2 | –24.5 |
| 10 | SB 1 | 1 | 99.0 | 1410 | 2800 | 708 | 919 | 1813 | 25.7 | 71.1 | +19.4 |
| 11 | SB 5 | 5 | 95.0 | 1390 | 2670 | 714 | 934 | 1836 | 24.7 | 66.0 | +2.6 |
| 12 | SB 10 | 10 | 90.0 | 1480 | 2540 | 722 | 954 | 1860 | 23.5 | 82.9 | –23.9 |
| 13 | FB 1 | 1 | – | 1460 | 7800 | 440 | 745 | 338 | 25.7 | 113.7 | –35.9 |
| 14 | FB 5 | 5 | – | 1230 | 7550 | 454 | 754 | 639 | 24.7 | 90.5 | –33.4 |
| 15 | FB 10 | 10 | – | 1430 | 7250 | 471 | 781 | 913 | 23.5 | 104.5 | –31.3 |
| 16 | FB 15 | 15 | – | 1540 | 6850 | 469 | 779 | 1113 | 22.2 | 125.2 | –24.4 |

* Remaining iron.

— wide development of production of ferrosilicon and its application almost in all grades of steel;

— ease of introduction of ferrosilicoboron into steel without changing its smelting technology.

Chemical composition of the obtained metal is presented in Table 2.

In this way, the proposed complex ferroalloy ferrosilicoboron has higher service characteristics than ferroboron or other boron-containing alloys, and ladle technology of its obtaining does not require special energy consumptions and smelting equipment, expensive raw materials; it differs by the ease and low production costs.

Industrial tests of the technology of microalloying of pipe steel grades with boron using a new complex ferroalloy—ferrosilicoboron, containing 0.9% B, 63% Si, the rest—Fe [2], which provides a sufficiently high degree of boron assimilation (up to 96%) without complicating the existing technological scheme, were carried out in ESPC OJSC “STZ”. At the same time during the whole time of ladle processing, the steel was characterized by stable content of boron.

The possibility of boron reduction from oxide system by carbon and aluminum of steel was theoretically and experimentally substantiated (direct alloying with boron). Test metal, microalloyed with boron using this method (0.0025–0.0035%), showed decreasing of the tendency of aging, increasing of the thickness of the dense skin of the ingot, reduction of the content of sulfur and phosphorus in steel, decreasing of the concentration of oxide and sulfide inclusions.

To form liquid highly basic slags with better refining properties, instead of fluorspar, materials with $B_2O_3$ were used. The results of laboratory experiments showed that slags of basicity of 5.0, containing 15–30% $Al_2O_3$, 8% MgO and 4% $B_2O_3$, in temperature range of 1500–1550°C are characterized by low viscosity, which does not exceed 0.15 Pa s. At the same time, holding of deeply deoxidized metal, containing 0.21% C, 0.79% Mn, 0.35% Si and 0.028% Al under the slag of the abovementioned composition at temperature of 1600°C, along with deep desulfurization, is accompanied by microalloying of steel with boron.

When using basic boron-containing refining slags, desulfurization degree of test metal deoxidized by aluminum and silicon, reaches on the average 22.2–23.1% against 12.5–16.7% on smelting of the

**Table 2.** Chemical composition of ferrosilicoboron

| Number of ingot* | Cr | Si | A1 | B |
|---|---|---|---|---|
| 1 | 0.50 | 64.70 | 0.80 | 0.91 |
| 2 | 0.50 | 64.50 | 0.80 | 0.84 |
| 3 | 0.30 | 63.40 | 0.90 | 0.91 |
| 4 | 0.20 | 65.00 | 0.80 | 0.78 |
| Average | 0.38 | 64.40 | 0.83 | 0.86 |

* Samples are taken from different ingots.

**Table 3.** Microelements consumption for steel processing and cost of improving its strength properties

| Indicator | | Element of ferroalloy | | | |
|---|---|---|---|---|---|
| | | niobium | vanadium | boron (FB17) | boron (FSB) |
| Price of 1 kg of element in ferroalloy on Russian market, rub. | | 1583 | 1250 | 1235 | 791 |
| Average content of element in steel | | 0.040 | 0.070 | 0.003 | 0.003 |
| Coefficient of assimilation of alloying element by steel | | 0.83 | 0.83 | 0.70 | 0.92 |
| Average consumption and cost of an element per 1 ton of steel | kg | 0.480 | 0.840 | 0.043 | 0.033 |
| | rub. | 760 | 1050 | 53 | 26 |
| Average improvement rates $\sigma_u$ at average element consumption* | | $\frac{6–8}{7}$ | $\frac{5–17}{11}$ | $\frac{3–10}{6}$ | $\frac{3–10}{6}$ |
| Element consumption per unit of increase of $\sigma_u$, kg | | 0.0690 | 0.0760 | 0.0070 | 0.0055 |
| Cost of increasing of a unit of $\sigma_u$ by microelement, rub. | | 109.20 | 95.00 | 8.60 | 4.35 |

* Numerator—limit values, denominator—mean value.

current production, which provides the sulfur content in steel at the level of 0.010–0.014%.

It was shown experimentally that the capability of obtaining liquid slag at the expense of introduction of $B_2O_3$ in it can be successfully applied for formation of highly-magnesium slags, which can significantly reduce the wear of magnesite lining of steel smelting units.

Comparison of the impact of niobium, vanadium and boron on the indicators of quality of steel was carried out and an attempt to give an approximate cost estimate of the efficiency of microalloying of steel with these elements was made [27]. The results of comparative analysis of averaged values of consumption of the microelements for processing and the cost of improvement of the steel properties are presented in Table 3.

The consumption of an element per a unit of increasing of $\sigma_B$ reflect the amount of the microelement required for increasing temporary resistance of 1 t of steel per 1 kg/mm$^2$ (10 N/mm$^2$). The increment cost of a unit if $\sigma_u$ by microelements characterizes the enterprise costs required for increasing the strength of 1 t of steel by 1 kg/mm$^2$ by various microelements.

According to computations, the most expensive microelement, used for increasing the strength properties, is niobium. Microalloying of steel with vanadium in order to increase the strength characteristics of metal without accounting special properties is also quite expensive. Boron was considered in the composition of traditional ferroboron (FB17) as well as the new alloy—ferrosilicoboron (FSB). Microalloying with boron is the cheapest of the listed. It is economically profitable to use ferrosilicoboron, the cost of boron in which is significantly lower, as the boron-containing alloy.

It can be assumed that qualitative conclusions regarding the costs of increasing the unit of both strength and other indicators of the service characteristics of steel will be in favor of microalloying with boron. This is evidenced by its consumption and the cost of microalloying, which is less than when using niobium and vanadium.

Thus, microalloying of a wide range of steels with boron-containing alloys is economically attractive. This is evidenced by the presence of stocks of raw materials, and a new, more economical and environmentally friendly technology for producing an alloy with boron, as well as the presence of a technology for introducing the latter into steel without changing the melting process.

Modern technological process of steel production, which includes smelting of an intermediate product in EAF and converters with further processing of steel in metal refinement units, obtaining of low-carbon ferrochromium are accompanied by formation of large amount of solid industrial wastes—metallurgical slags of lime-silicate composition [28].

The peculiarity of these slags is concluded in the fact that, during cooling, they are decomposed into fine-grained powder [29, 30]. The duration of decay varies from several hours to several days. Decay products are ecotoxic materials; they are easily aerated, spread over large areas, and dissolve in sedimentary and ground water.

One of the directions of stabilizing slags [31] from decay is replacement of anion $SiO_4^{4-}$ of dicalcium silicate with anion $BO_4^{5-}$, with its presence providing high fluidity in refinement slags.

Addition of borates to the slag during or immediately after separation of the slag and the metal are effective for stabilization for steel smelting slags and prevention of their decay [32].

Slag decay of stainless steel during cooling can be prevented by borate addition [33–35], which assumingly stabilizes high-temperature polymorphous phase by forming a solid solution with $2CaO·SiO_2$.

It was shown experimentally that the presence of more than 0.34% $B_2O_3$ in highly basic slags has a stabilizing effect on them.

A series of industrial experiments involving production of colemanite as boron-containing material was carried out to estimate the efficiency of the use of $B_2O_3$ as a stabilizer of slags of low- and medium-carbon ferrochromium against decay [36]. Computed content of $B_2O_3$ in the slag constituted 0.37–0.55% correspondingly. Sampling for chemical analysis was carried out from the solidified slag after it was removed from the bowl. High actual content of $B_2O_3$ in slag with assimilation about 98% was noted. After cooling, almost all the slags remained in a lumpy form, which did not disintegrate into powder.

It was shown that $B_2O_3$ in the form of various boron-containing raw materials is an effective stabilizer of highly basic slags of ferroalloy and steel smelting production, which allows obtaining marketable lump material at small consumption.

## CONCLUSIONS

The ways of using boron and its compounds in the processes of preparation and metallurgical processing of ore materials in order to improve the quality of the final products were considered. The developed technologies are provided with boron-containing raw materials. Theoretical, laboratory and industrial tests showed the possibility of increasing the technical-economical production indicators and the amount of pellets, agglomerates, cast iron, steel, ferroalloys and effective utilization of waste slags. The technical solutions put forward and tested at metallurgical enterprises do not require capital expenditures and are implemented by the addition of microdose of boron and its compounds to metallurgical production facilities.

The presented survey as well as the results of laboratory and industrial tests showed that boron and its compounds are applied in all redistributions of ferrous metallurgy, intensifying the processes and improving the quality of metal. Realization of the possibility of boron impact will positively affect the final complex of properties of metal production and slag.

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