Search for new compositions of boron-containing ferroalloys, their application and development of appropriate production techniques*

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ABSTRACT

Results of the present research aimed at search of the rational composition of new boron-containing ferroalloys containing 64-65% of silicon and 0.8 - 1.0% of boron and development of the efficient production technology of the alloys are presented. Cost-saving metallothermic method was proposed for ferro-silicoboron (FeSiB) production of borate raw and ferrosilicon. The boron reduction of boron-containing raw by high-silicon ferrosilicon (45 – 75 % of Si) was studied in the laboratory conditions. The investigation results testifies that the proposed composition of the boron-containing ferroalloy and its production technology are rather efficient. The obtained FeSiB was tested in a steel making: smelting in electric furnace and out-of-furnace treatment. It was established that the existing technological scheme for metal deoxidization by ferrosilicon is preserved when FeSiB is applied. Furthermore steel micro-alloying by boron can took place within the scheme, and the degree of boron digestion ranges up to 77.8-96.3%. It was noted the chemical composition of steel in respect of boron content was rather constant during the whole period of out-of-furnace treatment. For ferro-silicoboron the most admissible concentration of boron is 0.8-1.0%, such content ensures the level of boron percentage in steel in the range of 0.0025-0.0032% and no corrective procedures are required.

Keywords: *Boron, boron-containing ferroalloys, micro-alloying, reduction.*

1 INTRODUCTION

The perfecting of functional characteristics of steel is the most important task for steel makers. This consideration placed more stringent requirements upon the level of steel quality and properties consistency of steel output. At the same time a reduction of material costs and energy consumption are required for industry. Besides the claimed requirements upon the major functional properties of steel was increased by several times for the short period of time (about 5 years) [1].

Quality improvement should be performed at the every stage of steel making. The impact on quality of iron-carbon melt by alloying, modifying, refining, and deoxidizing is the key technique to manage steel quality.

In recent years the efficient techniques of steel microalloing and modification by ferroalloys containing V, Nb, B, Ca, etc. have received wide acceptance. Boron has a particular significance among these elements. Steel properties are capable to be affected by boron addition of ultra small quantities (0.001-0.003%). One should note that the steel properties are affected by boron in multi-functional way, namely, strength and plastic features, hardenability, and grain-boundary corrosion are changed, besides a broad assortment of steels (carbon, low-alloyed, corrosion-resistant, amorphous steels, etc.) can be treated by boron.

Steels micro-alloyed by boron did not find expanded applications in engineering and industry despite of the mentioned above advantages which are apparent. This is because of number of reasons. For example, expensive ferroboron (with boron content in the range of 15-20%) obtained by aluminothermic process from raw materials is used as the most widespread boron-containing ferroalloy. And normally, this ferroboron in the form of powder wires is added into steel using tribe-devices.

The present work is aimed at developing both the efficient compositions and the efficient production technology of the new boron-containing ferroalloys. Chemical composition and performance features of boron-containing ferroalloys have a significant impact on both the degree and consistency of boron digestion by liquid steel and the probability to fall within the narrow range (0.001- 0.003%) of boron content in steel.

The reported data [2-4] were taken into account to develop efficient boron-containing composition. The best results of steel micro-alloying by boron were obtained by its addition along with other chemically active elements (Al, Si, Ti, Mn, etc.) in the form of complex ferroalloy into melt. The major functions of the complex ferroalloy active components are to bind oxygen and nitrogen into strong compounds and to prevent their interaction with boron.

Due to the ultra-small boron content in steel it is advantageous to use complex ferroalloy with boron content decreased down to 1.0-2.0%. This provides a possibility of increasing the mass of boron-containing alloy introduced into steel along with improvement of its digestion degree and consistency.

The content of major components in boron-containing ferroalloy should be suited to the standard ferroalloys (e.g. ferrosilicon), what will provide a production optimization. Besides, the boron-containing ferroalloy should provide the required values of performance features influencing on its digestion. These major features are the density and the temperatures of melting onset and its completion.

The procedure for determination of the efficient ferroalloys composition was developed in the Institute of Metallurgy of the Ural Branch of the RAS [5]. The procedure where by values of density and the onset melting temperature (T_{on}) for ferroalloys are recommended to be in the range of 5000 – 7000 kg/m^3 and less than 1500 º C, respectively.

2 MATERIALS AND EXPERIMENTAL

The Fe-Si-B ferroalloy system characterized by high content of silicon and boron (within the ranges of 45-95% and 1-5%, respectively) was chosen for study. The alloy density was measured by picnometric technique. In the result of the measurements it was defined when alloy contains 23-60% of silicon the density takes on the recommended values, though the higher boron content, the lower the density is (Figure 1). The higher silicon content and the lower boron content in the melt, the lower the initial melting point (T_{on}) is (Table 1). The density value of the applied ferroboron (with boron content about 17-20%) for adding into steel is 5600-5800 kg/m^3, and T_{on}= 1450-1550º C.

The mentioned above physicochemical characteristics of the Fe-SI-B alloys systems containing 45-65% of Si and 1-3% of B are preferable in comparison with the ferroboron (17-20% of B) ones. Thus the ferro-silicoboron can be recommended for wide application in steel making.

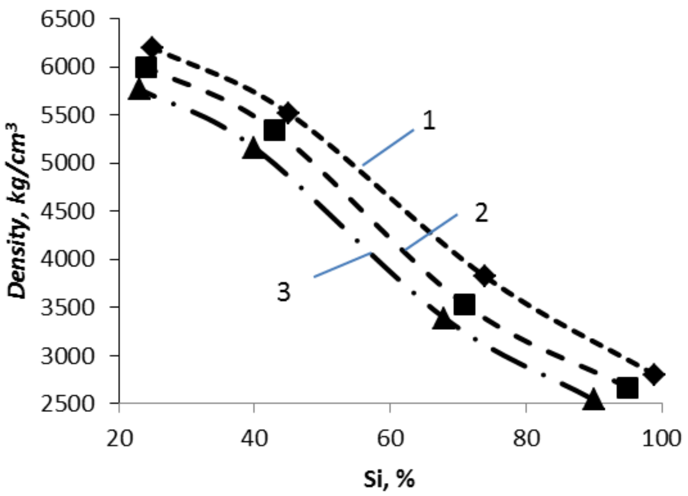

Figure 1: Influence of silicon and boron content on alloys density: 1 - 1%; 2 - 5%, and 3 - 10 % of boron.

Table 1: Onset melting temperatures of the Fe-Si-B alloys

Content, %		T_{on}, ºC	Content, %		T_{on}, ºC
Si	B		Si	B	
25	1	1395	74	1	1258
24	5	1418	71	5	1273
23	10	1443	68	10	1358
45	1	1275	-	-	-
43	5	1350	-	-	-
40	10	1400	-	-	-

In general, a melts mixing technique is applied to obtain complex alloys. Using of the technique is not efficient to obtain boron-containing ferroalloy, since this way requires an independent process of ferroboron production, namely, reduction smelting of borate ore.

Cost-saving metallothermic method was proposed for ferro-silicoboron (FeSiB) production out of borate raw and ferrosilicon. Ferroalloy with required composition is formed when boron oxides are reduced by high-silicon ferrosilicon taken in great abundance. The choice of the way is substantiated by the capability of boron-containing alloy production in the immediate time of ferro-silicon smelting by feed of boron raw materials into bucket during melt tapping. Hence the application of boron opens the way to a production of ferro-silicon with no significant changes of existing melting technology. The experiments of melting of boron-containing high-silicon ferroalloy were carried out in order to study a fundamental possibility of production of the complex boron-containing alloy based on the ferrosilicon by the proposed technique. For the melting test the ferrosilicon - type FS65 (64.5% of Si) as a deoxidizer and borate raw

(Colemanite) were used. The latter is comprised of hydrous calcium borate ($Ca_2B_6O_{11}\cdot 5H_2O$) and the share of B_2O_3 is about 40-50%.

Three types of Colemanite were used: 1) powder calcined at 600 ^{0}C with fineness less 0.5 mm (48% of B_2O_3); 2) calcined powder pelleted in tablets of 20 mm in diameter and 10 mm height (49% of B_2O_3); 3) powder fused at 1300 ^{0}C with fineness less 2.0 mm (42% of B_2O_3).

The experiments were conducted in crucible placed into electric furnace with graphite heater at the temperatures 1550, 1600, and 1650^{0}C. The charge of ferrosilicon and Colemanite was loaded into crucible. The weight of charge was in the range of 100 - 150 g, the weight was calculated in accord with stoichiometry required to obtain 2% and 4 % content of boron in the smelted alloy.

The melt was remixed and samples for chemical analysis were taken after 5, 10, and 15 min exposure.

The degree of boron transfer (K) into alloy was determined in the result of the tests.

K=[B]/{B}

where: *[B]* is the boron quantity in alloy; *{B}* is the boron content in Colemanite (in the form of B_2O_3).

3 RESULTS AND DISCUSSION

In the result of the present work the influence of time of Colemanite interaction with deoxidizer, the process temperature, the quantity and composition of introduced Colemanite on the alloy digestion degree of boron was studied. It was established the exposure time of melt at the constant temperature (1650^0 C) implies an significant increase in digestion degree of boron. As for the pelleted Colemanite the increase of melt exposure time from 5 to 15 min results in the increase of digestion degree from 44.7% up to 57.7%, and for sample of the calcined powder Colemanite leads to the increase from 48.0% up to 71.2% (Figure 2).

The temperature of melt has also significant impact on the reduction process. The temperature increase of ferrosilicon melt from 1550 to 1650^{o}C at the constant exposure time (10 min) and application of fused Colemanite has resulted in the increase of K on 9.4 %, and for samples obtained of calcined Colemanite the increase was on 14.0 %.

Assessment of the boron digestion degree in relation to the type of boron-containing raw was performed for the identical conditions: the temperature and the exposure time were 1650^{o}C and 10 min, respectively. The obtained results are listed in order of digestion degree increase: melted Colemanite 62.1%, pelleted Colemanite 66.3%, and calcined powder 71.2%. Such results may be attributed to the several reasons: there are variations of both the boron content in the different types of Colemanite and the rate of interaction between reducing agent and B_2O_3, as well as there are some losses of boron-containing materials.

When calcined Colemanite is fed into the alloy with 4% of boron calculated content the boron digestion is dropped by 7.4% in comparison with sample obtained of the same material but with 2% of boron calculated content.

Thus taking into account a quantity of fed material and its digestion degree the efficient boron content in the alloy is in the range of 1.0-2.0%.

Industrial trials to adjust the production technology of complex boron-containing ferroalloy based on ferrosilicon were carried out within Joint Stock Company Serov Ferroalloy Plant (Serov, Sverdlovsk region, Russia).

Calcium borate containing 35.6% of B_2O_3 and Colemanite as boron-containing material was applied. The calcium borate was obtained by commercial treatment of boron-containing raw materials. Boron-containing materials were fed into bucket immediately after metal pouring of previous temper. The material was warmed up and the metal was tapped from furnace into bucket subsequently. The composition of the produced ferroalloy (FeSiB) was 64-65% of Si, 0.6-0.85% of B, and the balance Fe.

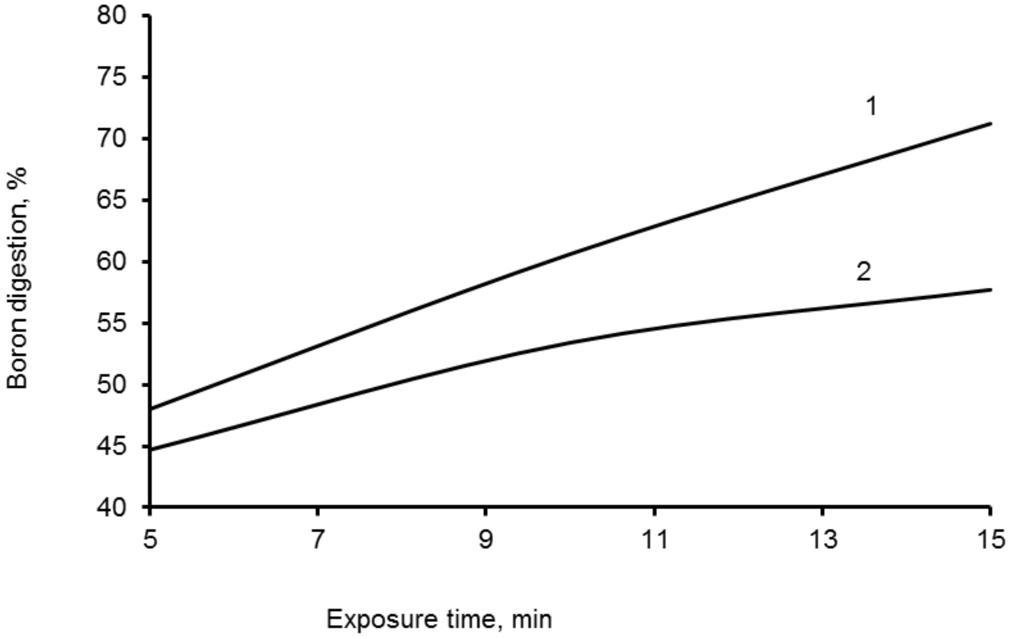

Figure 2: Relationship between the boron digestion and exposure time of melt at 1650°C and 2% calculated content of boron in alloy: 1 - calcined Colemanite in powder form; 2 - pelleted calcined Colemanite.

In the Experimental Steel Making Shop of Severskiy tube plant (Polevskoy, Sverdlovsk region) a pilot study were carried out to adjust the technology of boron micro-alloying of tube type steels. The steels were subjected to quenching and abatement using a new complex ferroalloy - ferro-silicoboron obtained in commercial conditions. The steel brands D, 32HGMRA, and 26HGMRA (26ХГМРА) were used for the tests. Deoxidization of metal, formation of refining slag, and steel micro-alloying by boron were carried out during tapping in bucket.

Relatively high degree of boron digestion varying in the range from 77.8 to 96.3% (86.6% is the average value) was provided by addition of ferro-siliconboron of the mentioned above composition, and no changes for the existing technological scheme of metal deoxidization are required. Besides the steel was characterized by consistency of boron content during the whole period of out-of-furnace treatment, namely, from the moment of metal deoxidization inbucket, during temper and tillcompletion of vacuum treatment, casting. At the unit of out-of-furnace steel treatment the boron percentage ranged up to 0.0021-0.0027% that provided the boron content in the metal during casting at the rate higher than 0.0020%. Mechanical properties of the pilot metal satisfied the requirements of technical regulations.

4 CONCLUSIONS

This work demonstrates a significant production potential of the proposed complex boron-containing ferroalloys using inexpensive borate raw within the existing production facilities. As for the present technological scheme of steel smelting, no changes are required when the *FeSiB* alloy is applied. Taking into account that essential quantity of boron as alloying element is many times smaller than other similar additives of the same purpose, therefore it is advantageous to increase a production volume of metal micro-alloyed by boron of a broad assortment, what results in an increase of consumption characteristics of the metal with minimum costs.

5 REFERENCES

[1] Uglov V.A., Zaitsev A.I. and Rodionova I.G. General lines of metallurgy technology development to meet the modern requirements in the level and stability of steel properties, Bulletin Ferrous metallurgy, 2012, №3, pp. 85-93 (in Russian).
[2] Popov V.P., Zayko V.P. and Zhuchkov V.I. Production and application of the complex boron-containing ligatures for steel making Theory and practice of production and application of complex ferroalloys. Mecniereba, 1974 pp. 245-250 (in Russian).
[3] Lukin S.V., Zhuchkov V.J., Vatolin N.A. The surface tension, density and oxidation kinetics of Fe-Si-B alloys / Journal of the Less-Common Metals.1979. V. 67. №2.pp. 399-405.
[4] Lyakishev N.P., Pliner Yu.L., Lappo S.I. Boron-containing steels and alloys, Metallurgy, 1986. (in Russian).
[5] Zhuchkov V.I., Noskov A.S. Dissolution of ferroalloys in liquid metals. UrD AS USSR, 1990.
[6] Stepanov A.I., Babenko A.A., Sychev A.V., Zhuchkov V.I. et al. Technology experience in steel micro-alloying by boron using ferro-silicoboron. Metallurgist. №7. 2014. pp. 50-52 (in Russian).