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Microalloying of low carbon steel with boron and a method for determining the effective concentration of dissolved boron

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Мікролегування низьковуглецевої сталі бором та спосіб визначення ефективної концентрації розчиненого бору

Goal. *The effect of boron on the properties of steel is considered. It has been established that hardenability improves due to the influence of boron, which is not bound in oxides, nitrides or other compounds. This boron is in solid solution in austenite and is called an "effective" boron. The mechanism of increasing the hardenability of steel due to such boron is associated with inhibition of the occurrence of crystallization centers of ferrite and bainite.* ***Methodology****.The effective fraction of boron in dissolved state in austenite is determined by the method of electrochemical phase analysis.*
The microalloying of low-carbon steel 08kp with boron is tested on industrial heats under conditions of Martin workshop of JSC «Zaporozhstal». Smelting and teeming of steel were performed according to the requirements of operating technology. The input of ferroboron into metal took place while letting out the heats into the ladle after completion of the ferromanganese input. All the experimental heats were blown through in the ladle with argon to appearance of the furnace slag. For microalloying the ferroboron of the grade FB20 was used.
At the by-sheet sorting of the experimental ingot of the heat (the average content of boron in the heat - 0,00138%), sampling of metal rolled stock was brought off on 5 horizons by the height. In every sample the chemical analysis for the content of boron was executed in 3th points, corresponding to the edge of roll, ¼ on the width and axis. Results of the chemical analysis are presented in the table 1. At the average content of boron in the heat - 0,00138%, the content of boron was distributed along the height and width of the ingot was distributed from 0,0008% (-0,00058%) to 0,0024% (+ 0,00102%).
Results*. The technology of microalloying low-carbon steel with boron has been mastered with obtaining a guaranteed content of at least 0,0008%. Putting a ferroboron into the ladle with a flow rate of 0.26 - 0.31 kg / t followed by purging the metal in a ladle with pure argon provides the boron content in the steel 0.0009 - 0.0015%. The absorption of boron during microalloying depends on the fractional composition of boron-containing material. For a fraction of less than 3 mm, assimilation is 29%, and for a fraction of 5-10 mm, 76% of the assimilation values obtained for an optimal fraction of 20-40 mm. Boron in 08kp steel increases the tensile strength by 4.5% and the yield strength by 2.6% compared with the average values of this steel without boron.*
Key words: *"effective" boron, mild steel, microalloying, hardenability*
Мета. *Розглянуто вплив бору на властивості сталі. Було встановлено, що прокалюємість поліпшується завдяки впливу бору, який не пов'язаний з оксидами, нітридами або іншими сполуками. Цей бор знаходиться в твердому розчині в аустеніті і називається «ефективним» бором. Механізм підвищення прокалюємості сталі за рахунок такого бору пов'язаний з пригніченням появи центрів кристалізації фериту і бейніту.* ***Методика.*** *Мікролегування низьковуглецевої сталі 08кп з бором випробовується в промислових умовах Мартінівського цеху ВАТ «Запорожсталь». Виплавку та розкислення сталі виконували відповідно до вимог експлуатаційної технології. Введення фероборону в метал відбувалося під час випуску металу в ківш після завершення введення феромарганцю. Всі експериментальні плавки металу продували в ковші аргоном до появи пічного шлаку. Для мікролегування використовували фероборон марки FB20. Під час сортування експериментального злитка тепла (середній вміст бору в теплі - 0,00138%) відбір проб металопрокату був знятий на 5 горизонтах за висотою. У кожному зразку хімічний аналіз на вміст бору проводили в 3-х точках, що відповідають краю валка, ¼ по ширині та осі. При середньому вмісті бору в металі 0,00138%, вміст бору розподілявся по висоті і ширині злитка від 0,0008% (- 0,00058%) до 0,0024% (+ 0,00102%).* ***Результати.*** *Ефективна частка бору в розчиненому стані в аустеніті визначається методом електрохімічного фазового аналізу.Технологія мікролегування низьковуглецевої сталі бором відпрацьована з отриманням гарантованого вмісту не менше 0,0008%. Завантаження ферробору в ківш з витратою 0,26-0,31 кг / т з наступною продувкою металу в ковші чистим аргоном забезпечує вміст бору в сталі 0,0009 - 0,0015%. Поглинання бору при мікролегуванні залежить від фракційного складу борвмісного матеріалу. Для фракції менше 3 мм асиміляція становить 29%, а для фракції 5-10 мм - 76% від значень асиміляції, отриманих для оптимальної фракції 20-40 мм. Бор в сталі 08кп збільшує межу міцності на розрив на 4,5% і межу плинності на 2,6% в порівнянні з середніми значеннями цієї сталі без бору.*
Ключові слова:ефективний бор, мікролегування, засвоєння, міцність

Introduction. The complex of valuable and various physical and chemical and other properties of the boron compounds is the basis, affording the wide use of the boron in all branches of industry. As to the variety of using fields, from all the elements of the periodic system the boron yields only to the carbon. The boron as an alloying element is known long ago, and many methods of improving the quality of ferrous and non-ferrous metals and special alloys by means of boron additions have use over a long period of time.

Analysis of literary data. The first systematic researches, putting beginning to the scientific study of the boron containing steel were done under the guidance of the future academician of the Academy of

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Sciences of the USSR Chizhevskij N.P. and were published in 1915 [1]. On the basis of results of thermal and chemical analyses and microstructure of obtained alloys, the diagram had been made up for alloys containing to 11,54% B. As a result of research compounds FeB and Fe_2B were found. Influence of the boron on the redbrittleness, hardness and malleability of steel had been studied. In 1942 -1944 the articles appeared presenting the results of research on the influence of small boron quantities in constructional steel, which were systematized and published in the paper [2].

In 1960 the book “Boron, its compounds and alloys” edited by G.V. Samsonov appeared in the publishing house of the Academy of Sciences of Ukrainian SSR [3]. In this book the description of all the known systems with participation of the boron is given, the questions of using the alloys of boron in manufacturing the heatproof alloys, radio engineering and electronics, machine-building, metallurgy and chemistry had been considered in detail.

In 1961 a monograph on the influence of the boron, calcium, niobium and zirconium in cast-iron and steel had been translated, edited by Vinarov S. M. [4]. It is noted in this paper that unlike the most of alloying elements the boron is added to steel in extraordinarily small quantities (10^{-4} 10^{-3}). On the other hand, additions of the boron must be restricted to some certain limits, because excessively small doses can appear not effective, and too large additions can result in fragility and redbrittleness of steel.

In 1975 continuation of the work by Samsonov G.V. has been published in the direction of studying the boron and in particular borides [5]. In this book the detailed analysis of existing data on the chemical structure and crystalline structure of borides of metals and non-metals had been performed, the questions of chemical connection and electronic structure of borides and nature of their physical, physical and chemical and chemical properties are considered. The diagrams of state for the systems of all the elements of the periodic system are considered with the boron, the characteristic of conditions of existence, formation and properties of double boride phases had been given. The methods of obtaining borides are described as well as the most important fields of using borides in industry and technique, and in scientific research too.

In 1983 Tkachev K.V. and Plyshevsky J.S. published the book on technology of inorganic compounds of boron in the publishing house “Chemistry”[6]. Physical and chemical properties, fields of use and source of raw materials of the major inorganic oxygen compounds of boron are considered in given book. Methods and technological schemes for manufacturing boron compounds from different raw material are presented. Physical and chemical basis of processes, equipment to be used, quality of products to be obtained have been described as well as the ways of utilization of waste.

In the work of the well-known metallurgist, academician of the Russian Academy of Sciences Lyakishev N.P. with colleagues published in 1986 information is generalized about boron-containing steels and alloys [7]. Physical and chemical properties of boron and its compounds with elements, entering the composition of steel had been considered. Influence of boron on properties of cast-irons, carbon and low-carbon constructional steels, corrosion-resistant and high-temperature steels and alloys had been studied. Chemical and analytical basis of measuring the mass share of boron in alloying alloys and steels have been expounded.

Solubility of B in αFe and γFe is very small. At temperatures 500 and 910°C no more than 0,001 and 0,13% (at.) of B is dissolved in αFe. At the temperatures 910 and 1150°C about 0,008 and 0,025% (at.) B is, accordingly dissolved.

In the Institute of casting problems of Academy of sciences of Ukraine under the direction of Braun M. P. the works had been conducted work in studying the influence of alloying elements on properties of steel and creation of economically alloyed steels for machine-building. The results of research are published in works [8-10]. In opinion of Braun M. P. the best complex of mechanical properties of steels (silica-manganese, silicon-chrome, chrome-manganese, chromium-manganese-siliceous and the other alloyed steels had been studied) can be attained by the complex alloying with strong carbide-forming and rare elements. The author came to the conclusion, that the joint influence of two carbide-forming elements on diminishing of size of grain is much more considerable, than separate one.

By the published data, at the content (10^{-4} 10^{-3}) the influence of boron on the hardenability and viscosity of low- and medium-alloyed steels corresponds to the result which can be got while alloying with chromium, manganese, molybdenum or nickel, only in 100-300 times exceeding additions of the boron. Introduction of the boron in complex with other alloying elements into the steel is especially effective. So, microalloying of the low-alloyed steels to be improved with boron creates possibility of providing the of good deformability simultaneously with high hardenability what resulted in the increase of using such steels [7].

Raising of problem. Important property of steel is its capacity for obtaining of maximal hardness at tempering. Depth of the hard-tempered layer with martensitic or martensite-troostite structure depends on many factors, including composition of austenite. All the elements, dissolved in austenite (with exception of Co), increase hardenability. The special role in these processes belongs to boron. None of these elements, at the content about 0,0005%, cannot be compared with B as to efficiency. Not the whole boron influences on hardenability, but only that part of boron, which is unbound in oxides, nitrides or in other compounds, and is in the solid solution in austenite; it is so-called «effective» boron. At the content less than 0,007% boron increases appreciably hardenability of steel , and it renders no harmful influence on other properties. Therefore steels containing 0005-0,007% boron, have an important industrial value.

The rapid introduction and wide use of such steels abroad is explained mainly by financial viability, as there is no more necessity of introducing alloying elements used earlier. The mechanism of increasing hardenability of steel due to boron is connected with braking the originating of crystallization centers of ferrite and bainite. According to modern theories [11], the mechanism of hardenability of steels is explained by concentrating of boron on the borders of grains of austenite before the beginning of transformation.

In liquid steel the boron unites easily with oxygen, nitrogen and other admixtures. If this interaction is not prevented, it will not remain free boron in steel. For maintenance of part of boron in the free state during melting, before addition of boron, steel must be fully desoxydated by aluminium, and at the considerable content of nitrogen, before addition of boron or together with it, it is necessary to add nitride-forming elements (titanium or zirconium). Taking into account that boron in the furnace usually oxidized and removed to slag, in the productive melting the boron is almost always added to the ladle. Application of the boron is the most perspective for steel of EAF method of production, containing the least amounts of oxygen, sulphur, phosphorus and other admixtures.

One of reasons, braking, to az certain time, wideuse of the boron for the improving hardenability of steel products was difficulty in determining the thousandth and tenthousandth percents of boron and, especially of its free part. If presently the problem of determining of general content of small quantities of boron in steel is practically solved (in 2012 GOST [12], allowing relatively simple to determine in steel from the 0,0001% B and more), determination of the content of effective boron requires introduction on the metallurgical plants of Ukraine of the special physical and chemical methods of phase analysis. Absence to the last time of such methodologies, in a certain measure, brakes development and introduction of application of boron in steel-smelting processes in Ukraine.

Determination of the microquantities of the boron is related to overcoming of a number of chemical and metallurgical complications. At first, with high chemical affinity of boron to oxygen and nitrogen (it is easily oxidized and associates in nitrides and oxides in fusion), and secondly, with that in most cases it is required to provide very small content of boron in steel and in narrow limits. Long-term practice of application of standard ferroboron for microalloing steels showed, that it did not provide stable results even at the special technology of desoxydating and degassing. The complex boron-containing ligatures, simultaneously including strong desoxydating and degassing elements along with the boron, are more effective in application. However, neither in Ukraine nor in Russia such alloys are not produced. The production of complex alloys is mastered abroad for the microalloying of steel with boron, such as Grainal, Bast and other. They are characterized by low content of boron and high price. Therefore their application becomes frequently economic unprofitably.

In the Magnitogorskij state technical university the new technology for obtaining the boron-containing alloying alloys on the basis of borides in the mode of self-propagating high temperature synthesis (CBC) had been developed and introduced under conditions of Magnitogorskij metallurgical integrated works and financial and technological viability of application of such alloys is shown for the microalloying of steel with boron instead of standard ferro-alloys [13].

Determination of boron fraction of (0,0005 - 0,0070% B), being in metallic solution, with a chemical method is connected with some complications. It is necessary to separate this microquantity of boron from the residue of nitrides, carbides, oxides and borides. Free energy of formation of these compounds is more than free energy of formation of the solid solution of boron [14]. It allows to separate the «effective» boron by means of electrochemical phase analysis.

Experimental research of determining the microquantities of boron.

While performing analysis one distinguish sometimes the soluble and non soluble in acids part of boron, assuming [11], that efficiency of the boron is determined by its soluble part. From some data [11], soluble as well as non soluble in acids part of the boron influences the hardenability of steel, and distinction between them is caused by methodology of chemical analysis.

Practically in all accessible to us in the last few years articles, dissertations and patents, related to the influence of the boron on hardenability of steel, usually is not reported about determining the quantity of boron, being in the solid solution. Only data about the content of general boron and increase of the steel hardenability are oresented. To our opinion, it is reached at the account of the fact that the liquid steel had been preliminary so cleared by metallurgical methods, from oxygen and nitrogen, that the remaining boron, unbound in nitrides, carbides and oxides, appeared in the solid solution. However nothing is reported about economic expenses of such treatment. It is possible that the effect of increasing hardenability at the expense of effective boron would be more meaningful. But the absence of information about the amount of boron in effective fraction does not allow to predict the improvement of the steel hardenability due to influence of boron.

All of this assisted the necessity of developing physical and chemical methodology of determining the amounts of the effective boron. As the uneffective part of boron can be related to nitrides, oxides, carbides and borides, it was necessary to find such electrolyte where these compounds would not dissolve. Such solvents could be the weak acids.

There are no data dependence between the type of boron compounds in steel and their solubility at the treatment of steel with different electrolytes. There is information only about clean chemical compounds. So, nitrides and carbides of the boron under normal terms do not dissolve in diluted acids. Fe_2B and FeB, though being dissolved in HCl, HNO_3 and H_2SO_4, especially in hot concentrated solutions, almost do not dissolve in H_2O at boiling.

We are set [15], that at the electrochemical dissolution of low-alloyed steels it is possible to dissolve the metallic basis of steel, leaving in safety different compounds of nitrides, carbides and oxides. It is related to that they are more steady as to thermodynamics, than metallic basis. Compounds of boron are not exception. At the same time, it allows to extract the boron fraction at electrolysis into electrolyte.

Rapid introduction and wideuse of the boric steels in 1937 - 1952 are explained mainly by the necessity of economy of alloying elements. Development and introduction of the boric steels became there possible since one learned to control the amount of effective boron and to find correlation between its content and obtained hardenability.

One of the variants [16] had been used to solve the problem of determining the effective boron. The effective boron in the solid solution of steel is separated from the boron bound in oxides, nitrides and other compounds by means of electrochemical method of the phase analysis. The content of effective boron is determined according to GOST, [12] as well as the general content of boron in electrolyte, got after electrolysis. This methodology [17] was approved on Nizhnedneprovskiy Pipe Rolling plant. The chemical composition of the steel under investigation after the data of the plant (the common content: % mas): 0,24% With, 0,53% M, 0,09% Si, 0,012% P, 0,020% S, 0,09% Cr, 0,04% Ni, 0,03% Cu, 0,037% Al, 0,002% Ti, 0,003% B. After the data of NMetAU: the content of the general boron is of 0,0024% and the content of effective boron is of 0,0010% B. The use of the offered methods extends the possibility of development and introduction of the new high-quality boron-containing steels.

Results of industrial tests. The microalloying of low-carbon steel 08kp with boron is tested on industrial heats under conditions of Martin workshop of JSC «Zaporozhstal». Smelting and teeming of steel were performed according to the requirements of operating technology. The input of ferroboron into metal took place while letting out the heats into the ladle after completion of the ferromanganese input. All the experimental heats were blown through in the ladle with argon to appearance of the furnace slag. For microalloying the ferroboron of the grade FB20 was used.

At the by-sheet sorting of the experimental ingot of the heat (the average content of boron in the heat - 0,00138%), sampling of metal rolled stock was brought off on 5 horizons by the height. In every sample the chemical analysis for the content of boron was executed in 3th points, corresponding to the edge of roll, ¼ on the width and axis. Results of the chemical analysis are presented in the table 1. At the average content of boron in the heat - 0,00138%, the content of boron was distributed along the height and width of the ingot was distributed from 0,0008% (-0,00058%) to 0,0024% (+ 0,00102%).

Table 1. Content of the boron in metal rolled stock by horizons

№ of sample	**Content of boron, %**			
	axis	**1/4**	**edge**	**Average value**
1 (bottom)	0,0009	0,0008	0,0010	0,0009
2	0,0011	0,0011	0,0012	0,0011
3	0,0012	0,0017	0,0015	0,0015
4	0,0015	0,0024	0,0013	0,0017
5 (top)	0,0014	0,0012	0,0013	0,0013
Average	0,0012	0,0014	0,0013	0,0013

In the course of the work it was noted that assimilation of the boron from a ferroboron is unequal and depends on the method of input and largeness of ferroboron. On the Fig. 1 the results of analysis of the boron assimilation are presented depending on the fraction of ferroboron (mm).

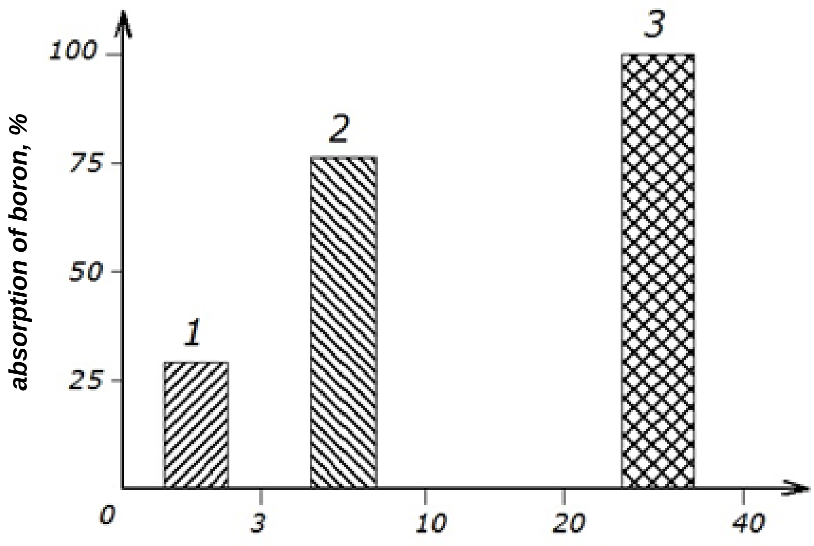

Fig.1 *Assimilation of the boron depending on the fraction composition of FeB*,%*
** assimilation of FeB by the fraction 20-40 mm is accepted for 100%.*
1 – fraction 0-3 mm; 2 - fraction 5-10 mm; 3 - fraction 20-40 mm.

At the control and acceptance tests of mechanical properties in production line on all the batches results were obtained as to ultimate strength and relative elongation conforming to requirements GOST 16523-97 "Thin-sheet rolled products from carbon steel of high-quality and usual quality of general purpose". Yield stress for steel of the got grades is not normalized. Tests on the cold bend are satisfactory. Mechanical properties of all the tested samples satisfy the requirements GOST 16523-97 for rolled metal products of steel of the grade 08kp (group of durability К260В), thickness of 2,8mm.

Conclusions.

1. Hardenability is improved at the expense of the influence of not the whole boron, but only of that part of its, which is unbound in oxides, nitrides or in other compounds, but is in the solid solution in austenite; it is so-called «effective» boron. The mechanism of increasing the hardenability of steel at the expense of such boron is connected with braking the origin of centers of the ferrite and bainite crystallization

2. Possibility of determining the effective fraction of boron, being in dissolved state in austenite had been established. Free energy of formation of the solid boron solutions is smaller than free energy of formation of nitrides, carbides, oxides and borides, that enables to separate the «effective» boron by electrochemical phase analysis.

3. Under conditions of the Martin production of JSC «Zaporozhstal » the technology of microalloying the low-carbon steel with boron had been mastered with obtaining the guaranted content at level no less than 0,0008%. Input of ferroboron into the ladle with consumption of 0,26 - 0,31кg/t (65 – 75kg/ladle) with the subsequent blow of metal in the ladle with the pure argon assures the content of boron in steel of 0,0009 - 0,0015%.

4. Assimilation of the boron at microalloying depends on fraction composition of boron-containing material. Assimilation of ferroboron in fraction less than 3mm makes 29%, and in fraction of 5-10mm - 76% from the values of assimilation, obtained for optimal fraction 20-40mm. The boron in the steel 08kp increased the ultimate strength by 4,5% and yield stress by 2,6% as compared to the average indices of this steel without boron.

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