

BORON MICROADDITIVES EFFECT ON HEAT RESISTING PROPERTIES OF Cr-Ni-Fe BASED ALLOY

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Preliminary Note – Prethodno priopćenje

The introducing of boron in very small amounts (0,001 – 0,02 %) improves considerably wear resistance and hardness, raises hardenability and thermal stability, it promotes grain crushing [1-3]. A preliminary analysis of the natural phases identified certain phases such as $(\text{Nb, Mo})_2\text{B}$. It is also possible to assume the formation of boron-containing iron-based eutectics and complex carbon-boride phases based on chromium.

Keywords: Cr-Ni-Fe based alloy, boron microadditives, heat treatment, mechanical properties, microstructure

INTRODUCTION

A positive effect of boron microadditives on the properties of steel are rather well studied. In some works it is noted that microalloying with boron also promotes increasing plasticity [4, 5] due to forming a fine structure. Boron effect can be classified into two groups:

- in the first case boron effect is shown in forming complex strengthening phases that are allocated on the borders of grains and obstructing the borders movement, therefore improving thermal stability, wear resistance, etc.;
- in the second case boron effects the crystallization process as the horophilic element increases the speed of forming centers of crystallization, increases crystallization speed that leads to forming a fine-grained structure.

Practically in all works that deal with studying the boron effect on the properties of steel it is noted that the optimum content of boron in steel is its contents that does not exceed the value of extreme solubility of boron in iron, i.e. up to 0,15 % by weight.

Proceeding from these positions, practically all recommendations of the positive boron effect lead to microalloying since increasing the content of boron over the specified limits leads to forming rough coarse boron-containing phases on the borders of grains that leads to embrittlement and decreasing the effect strength. It should be noted that the specified tendencies of boron effect are considered on the example of steels with different contents of carbon.

Meanwhile, in works [5, 6] it is shown that increasing boron content ranging from 0,85 to 1,15 % effects positively the limit of long-time strength of the alloy based on the Cr-Ni-Co system (0, 40 % C; 1,2 % Mn;

0,40 % Si; 20 % Cr; 20 % Ni; 4 % Mo; 4 % W; 4 % Ni and Ta; 2 % Fe; the rest is cobalt) due to changing the alloy microstructure and forming new phases.

In the studies carried out earlier [7] boron effect on the heat resisting properties of the Cr-Ni-Fe system based alloy has been investigated. It has been shown that increasing the content of boron beginning with 0,5 % to 1 % effects positively the limit of long-time strength at the temperature 700°C. The subsequent increasing the boron content leads to decreasing the limit of long-time strength and embrittlement of the alloy. Increasing the limit of long-time strength is connected with forming the $(\text{Nb, Mo})_2\text{B}$ phase and complex carbon boride phases.

In work [8] it is noted that with microadditives in the complex alloys the effect of boron in the amount of 0,001-0,0025 % is equivalent to the effect of addition of 1,33 % Ni + to 0,31 % Cr + 0,04 % Mo; the effect of 0,002 % B on hardenability is equivalent to the effect of 1,5 % Ni.

For verification of this provision for the purpose of reducing in the alloy of scarce nickel and simplifying the technology of smelting the alloy there has been studied the boron microadditives effect on the limit of long-time strength of the experimental alloy. The amount of boron in the alloy varied from 0,005 to 0,5 %. The composition of the initial alloy without introducing boron is specified in Table 1. The alloy has been developed at the Center of Heat Resisting Materials at KSTU and has shown rather good results when tested for long-time strength at temperatures 700-800 °C.

It is known that boron is a chemically active element [1]. It has a very high affinity to oxygen and nitrogen and therefore easily interacts with even insignificant amounts of these elements, forming oxides and nitrides at small concentration of oxygen and nitrogen. In this regard the main objective when alloying with boron is to raise the extent of its assimilation, i.e. forming the conditions at which boron not only forms complex phases of introducing but also enters the solid solution.

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EXPERIMENTAL STUDIES

Equipment and tools

Most often the alloying with boron is carried out by means of ferroboration that contains a considerable concentration of boron (ferroboration of FB20 grade contains about 20 % of boron), but the extent of its assimilation in this case makes about 30 % [8]. It is most favorable to use the complex ligature containing aluminum and titanium. Aluminum is entered as a strong deoxidant, titanium is entered into the alloy for prevention of forming boron nitrides, and it is noted that the optimum ratio of Ti:B is to make 15:1. Using such a complex ligature permits to raise the extent of boron transferring to the solid solution up to 93-94 %. As the experimental alloy already contains enough aluminum and titan, in this case for alloying there is used FB20 grade ferroboration, its structure is presented in Table 1.

Table 1 Chemical composition of FB20 ferroboration / wt. %

Alloy	Experimental alloy	Ferroboration
C	0,065	0,05
Cr	44,9	-
Ni	35,94	-
Fe	rem	75,5
Mo	0,95	-
Nb	1	-
Ti	4,145	-
Al	3	3
Si	-	2
B	-	22
S	0,015	0,01

The amount of ferroboration for alloying has been calculated proceeding from the extent of 85% boron assimilation. In this case there is some contradiction with the data [9], but since thermal stability is mainly reached due to forming the phases of introduction, boron effect is shown not only as a part of the solid solution, but also as a part of strengthening phases, i.e. in total.

The pilot melting has been carried out in the induction UIP-25 furnace. The weight of one melting made 4.5 kg. The temperature of pouring has been controlled by means of the platinum-rhodium thermocouple and supported at the level of 1600°. Before charging chrome and then, just before pouring, there has been added aluminum ferrosilicon as a deoxidant. Boron has been entered in the form of FB20 ferroboration.

Precision casting of samples for long-time strength testing has been made by means of the usual melted paraffin model. For smelting paraffin the molds have been heated and kept at the temperature 150°. Before pouring the molds have been heated up to 600°. The castings have been cooled in the air at the room temperature. After cleaning the samples have been checked for foundry defects, the final shaping-up of the samples surface has been carried out by machining.

After smelting the obtained samples have been checked for the chemical composition (Table 2).

Table 2 Chemical composition of the obtained samples / wt. %

alloy	1 (reference)	2	3	4	5	6
C	0,06	0,062	0,062	0,063	0,063	0,063
Cr	43,8	43,7	43,84	43,7	43,67	43,75
Ni	35,8	35,95	35,87	35,96	35,89	35,82
Fe	rem	rem	rem	rem	rem	rem
Mo	0,85	0,95	0,86	0,92	0,94	0,963
Nb	0,98	0,95	1,011	0,97	0,98	0,995
Ti	3,65	3,75	3,89	3,88	3,92	3,94
Al	3,2	3,1	3,22	3,25	3,28	3,21
Si	0,94	0,98	0,96	0,94	0,96	0,956
B	-	0,006	0,022	0,087	0,215	0,495
S	0,015	0,015	0,015	0,016	0,016	0,016

The ready samples have been exposed to heat treatment in the mode: holding within 2 hours at 1100 °C with the subsequent aging within 4 hours at 700 °C.

After heat treatment the samples have been tested for long-time strength at the temperature 700 °C within 100 hours. The results are presented in Table 3.

Table 3 Results of long-term strength tests

Sample no.	Boron content / %	Long-time strength, σ_{100}^{700} / MPa
1	-	469
2	0,006	465
3	0,022	470
4	0,087	466
5	0,215	476
6	0,495	498

The Figure 1 shows the experimental regression line (curve 1).

The calculated regression line (curve 2) is constructed from equation $y = 2,6786x^2 - 13,779x + 481,6$ with a confidence factor $R^2 = 0,9143$.

RESULTS AND DISCUSSION

As can be seen from the data in Table 3, introduction of boron microadditives up to 0,5 % practically does not affect the long-time strength. Only an increase in boron content to 0,495 % leads to a marked increase in the long-term strength by 9,4 %, from 469 to 498 MPa in comparison with the sample.

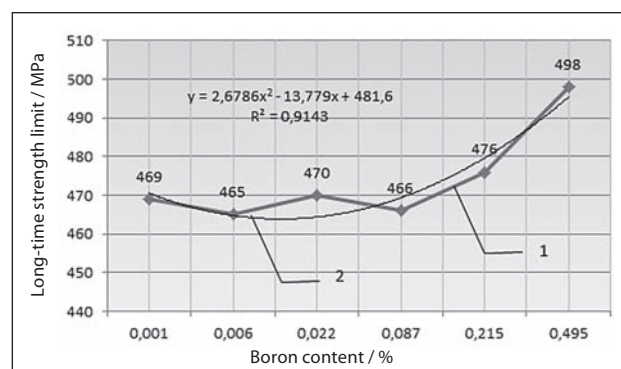


Figure 1 Dependence of the long-time strength on boron content

The absence of effect when introducing boron microadditives in a given alloy can be explained by the following circumstances. In the examined studies, the beneficial effect of boron microadditives was manifested, mainly, in steels. In the experimental alloy there is a high content of chromium, other elements are also present that form complex strengthening phases – Ti, Nb, Mo, Al, whose content is several times higher than the amount of boron introduced. Apparently, in this alloy the effect of influence of boron microadditives on the long-time strength is negligible compared to the effect of the strengthening phases. Only in the case of an increase in boron content of almost up to 0,5 % we may observe a noticeable increase in the long-term strength. An increase in the boron content up to 0,5 % is almost 5 times higher than the solubility limit of boron in iron, so with an excess of boron content that is excessive in comparison with the limiting solubility, the formation of boron-containing interstitial phases is inevitable, and they increase the limit of long-term strength.

In this connection, the microstructure of alloys with the boron content 0 %, 0,006 %, 0,215 % and 0,495 % (samples 1, 2, 5 and 6 respectively) have been investigated. The microstructure of the standard, i.e. sample without doping with boron, is represented by an austenite matrix with inclusions of a complex carbide phase of the type (Fe, Cr) $23C_6$, (Nb, Mo) C, Ti $3Al$ [1, 6]. These phases are hardener phases which determine the ultimate strength of the alloy Figure 2.

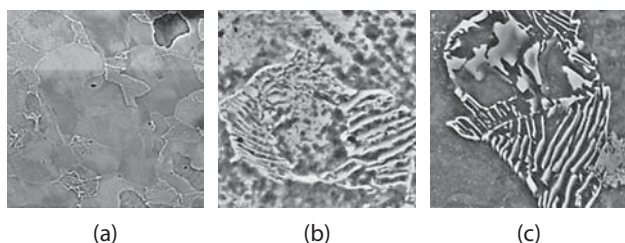


Figure 2 Microstructure of alloys with different boron contents a) 0 %; b) 0,006 %; c) 0,215 %, X 5 000

In alloys with 0,006 % and 0,215 % boron, the microstructure is not fundamentally new, the matrix is represented by an austenite-like phase with inclusions of the interstitial phases. A small difference is observed in a more distinct structuring, which was noted earlier [5]. This obviously shows the influence of boron, which, as is known, promotes the nucleation of crystallization centers. This can explain the lamellar structure by the type of perlite in individual sections of the microstructure.

The structure of sample No. 6, boron content 0,495 % (Figure 3), is slightly different. A sufficiently large number of interstitial phases (a), a clearly defined structuring, clearly defined boundaries are observed, which is due to the accumulation of interstitial phases. A preliminary analysis of the natural phases identified certain phases such as (Nb, Mo) $_2B$. It is also possible to

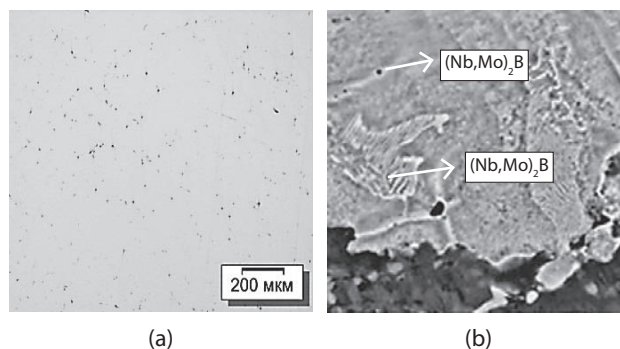


Figure 3 Microstructure of the alloy with 0,495 % B a) X 200, non-etched; b) X 500 after etching

assume the formation of boron-containing iron-based eutectics and complex carbon-boride phases based on chromium.

CONCLUSION

The carried out tests have shown that introducing boron microadditives up to 0,5 % does not practically effect the long-term strength of the Cr-Ni-Fe based alloy. Introducing boron with an increased chromium content as a microalloy into alloys based on this system is advisable for improving the quality of the alloy as a whole, but we should not expect an improvement in heat resistance as in case of heat-resistant steels.

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Note: The responsible for England language is Nataliya Drag, Karaganda Kazakhstan