Low-temperature formation of boron-containing layers and coatings by electron-ion-plasma method

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Abstract. Saturation of the surface of metals and alloys with boron is one of the promising methods for improving the service characteristics of the material. The aim of the present work is to analyze the elemental and phase composition, the state of the defective substructure of the surface layer of high chromium steel, which has been saturated with boron atoms under combined treatment conditions. It has been shown that low-temperature (653 K) ion-plasma borating allows forming a multilayer structure with a total thickness of up to 15 μm, containing nano-sized borides of iron and chromium. The hardness of the «film (B)/substrate (AISI 304 steel)>> system was increased by 2.2 times relative to the steel in the initial state; hardness of «film (B)/substrate (AISI 310S steel)>> system exceeds hardness of initial steel by 1.2 times. The «film (B/W)/substrate (steel)>> system is formed and melted with an intense pulsed electron beam. The formation of nanoscale particles of borides and carboborides of iron and chromium was revealed. It is shown that the hardness of the «film (B/W)/substrate (AISI 304 steel)>> system after irradiation with an electron beam is 1.5 times lower than the hardness of steel in the initial state; hardness of the «film (B/W)/substrate (AISI steel 310S)>> system - 2.3 times.

1. Introduction
Boron atoms have a high capacity to absorb neutrons and are therefore used as an alloying element in steels used in the manufacture of containers for storing spent nuclear fuel [1, 2]. The presence of boron atoms in steel leads to the formation of borides, which is accompanied by an increase in the strength, hardness [3, 4] and, often, brittleness [5, 6] of the material. Increased plasticity of boron-containing steels is achieved by additional alloying with titanium [7] and zirconium [8], spheroidisation of borides [9, 10]. An alternative, in some cases, to volume alloying is surface alloying, i.e., forming a surface layer enriched in atoms of alloying elements, including boron atoms.

One of the methods of surface alloying of steel implemented in the present work is a complex effect that combines, in various sequences, deposition of a film of an alloying element and irradiation with an intense pulsed electron beam. In a number of works performed on various materials, it is shown that such combined treatment allows forming in the surface layer a multi-element multiphase submicro- nanoscale structure with high strength and tribological properties [11, 12]. The volume of the specimens retains the plastic properties at the initial material level.

The aim of the present work is to analyze the elemental and phase composition, the state of the defective substructure of the surface layer of high chromium steel, which has been saturated with boron atoms under combined treatment conditions.
2. Material and methods

Stainless steels of AISI 304 grade (0.08C-2Mn-0.045P-0.03Si-(18-20)Cr-(8-10.5)Ni, the rest - Fe, wt%) and AISI 310S (0.2C-1Si-2Mn-(17-20)Ni- (22-25)Cr-0.02S-0.035P, the rest - Fe, wt%) were used as the study material. The specimens were in the form of plates with dimensions of 10x10x5 mm. The formation of a boron film on the surface of steel was carried out by plasma-assisted RF-sputtering of a cathode from boron powder at the following process parameters: magnetron power W = 0.8 kW, frequency f = 13.56 MHz, specimen temperature 653 K, process duration t = 1 hour; argon pressure p = 0.55 Pa, current of plasma generator with thermionic cathode (PIN-K) I_p = 100 A, bias voltage U_{bs} = 950 V, bias frequency 50 kHz. Specimens were under floating potential (heating of boron cathode from PIN-K anode). Before forming the boron film, the surface of the specimens was subjected to mechanical grinding and polishing; after placement in vacuum chamber and subsequent pumping - additional short-term (15 min.) argon plasma etching. A 0.2 μm thick tungsten film was deposited onto the specimens with boron film at the following process parameters: pulsed magnetron W = 0.2 kW, f = 60 kHz, I_p = 10 A, p = 0.3 Pa, t = 4 min. Irradiation of the «film/substrate» system with an intense pulsed electron beam was carried out at the SOLO setup [13] at the following process parameters: energy of accelerated electrons 18 keV, energy density of electron beam 25 J/cm^2, pulse duration 150 μs, number of pulses 3, pulse repetition frequency 0.3 s^{-1}, residual gas pressure (argon) 0.02 Pa.

Researches of element and phase composition, condition of a defective substructure carried out by methods of the transmission electron diffraction microscopy (JEOL JEM-2100F, Japan). The test objects (150-200 nm thick foils) for the transmission electron microscope were manufactured by ion etching (argon) of plates cut perpendicular to the surface of the specimen on an Ion Slicer (EM-09100IS). The microhardness of the «film/substrate» system was determined by a Vickers scheme on a DUH-211S nanohardness tester (Shimadzu, Japan) at a load of 1 mN and 5 mN.

3. Results and discussion

Deposition of boron film by method of plasma-assisted RF-sputtering of cathode from boron powder, regardless of the grade of the steel under study, leads to formation of multilayer structure, characteristic image of which is given in figure 1.

![Figure 1. TEM image of the structure of the «film (boron)/substrate (AISI 304 steel)» system. Designated: 1 - boron film; 2 - transition layer; 3 - the main volume of steel; the arrows are indicate the intermediate layer.](image-url)

The actual boron film (figure 1, a, indicated by 1) is separated from the main volume of the specimen by two layers. From the side of the boron film, a thin (15-20) nm intermediate layer was detected (figure 1, the layer is indicated by arrows). On the volume side of the specimen is a transition layer with a thickness of (100-130) nm (figure 1, a, indicated by 2). Then follows a layer of thermodiffusion conversion of steel up to 10 μm thick (figure 1, a, indicated by 3).
Phase analysis of the «film/substrate» system performed by transmission electron diffraction microscopy using a dark-field technique showed that the intermediate layer contains nanosized (2-4 nm) particles of iron and chromium borides of FeB, Fe2B, CrB6 composition located in an amorphous boron film. Transition layer is formed by nano-sized (30-45 nm) grains and sub-grains of solid solution based on γ-iron. Particles of iron and chromium borides of Fe3B, Fe23B6 and Cr2B composition were detected in the volume of the transition layer. Layer of thermodiffusion conversion of steel contains (FeNi)23B6, CrB and Fe3Ni3B particles, whose dimensions vary within (2-3) nm (figure 2). Obviously, the reason for the formation of the intermediate layer is the diffusion penetration of iron and chromium atoms into the adjacent steel volume of the boron film, followed by the formation of boride particles. Formation of boride particles in transition layer and layer of thermodiffusion conversion of steel is caused by penetration of boron atoms into surface layer of specimen with subsequent formation of particles.

![Image](image.png)

**Figure 2.** TEM image of the structure of the thermodiffusion layer formed during the deposition of the boron film (in figure 1, the layer is indicated by 3); \(a\) – bright field; \(b\) – SAED obtained from area of foil shown in \((a)\); \(c\) – dark field obtained in reflex [531] \((\text{FeNi})_{23}\text{B}_6\) (reflex is indicated by arrow on \((b)\)). Steel AISI 310S.

Mechanical tests were performed and an increase in hardness (load on the indenter of 1 mN) of the «film (B)/substrate (AISI 304 steel)» system relative to steel in the initial state by 2.2 times was detected. The hardness of the «film (B)/substrate (AISI 310S steel)» system exceeds hardness of initial steel by 1.2 times.

Irradiation of the «film (B/W)/substrate (steel)» system with an intense pulsed electron beam in the indicated mode led to high-speed melting and subsequent high-speed crystallization of the surface layer of the material. As a result of treatment, a multi-element multiphase weakly oriented banded structure is formed in the surface layer of steel (figure 3, a, b). The transverse dimensions of the bands vary in the range of 400-500 nm. Analysis of the microelectron diffraction pattern obtained from this structure (figure 3, c) indicates that the bands are formed by a solid solution based on FCC crystal lattice of iron (figure 3, d). The volume of the bands contains nanosized (5-10 nm) particles of iron boride of FeB composition (figure 3, e). Particles of the second phase are also observed at the boundaries of the banded structure (figure 3, e). Particles sizes range from 15 nm to 25 nm. The analysis of the microelectron diffraction pattern shows that these particles are carboborides of \((\text{FeCr})_{10}\text{(CB)}_6\) composition.

Mechanical tests were performed and a decrease in hardness (load on the indenter of 5 mN) of the electron beam irradiated «film (B/W)/substrate (AISI 304 steel)» system relative to steel in the initial state by 1.5 times was detected. The hardness of «film (B)/substrate (AISI 310S steel)» system is 2.3 times lower than hardness of initial steel.
Figure 3. TEM image of the surface layer structure of the «film/substrate» system irradiated with a pulsed electron beam; a, b – light fields; c – SAED obtained from area of foil shown in (b); d-f – dark fields obtained in reflexes [220]γ-Fe, [002]FeB and [220](FeCr)$_{23}$(CB)$_6$. Indicated on (c), reflexes 1 – [220]γ-Fe; 2 – [002]FeB; 3 – [220](FeCr)$_{23}$(CB)$_6$. Steel AISI 310S.

4. Conclusions

The mode was revealed and formation (by plasma-assisted RF-sputtering of a cathode from boron powder) of a boron film up to 500 nm thick on the surface of high-chromium steel was carried out. Microdiffraction analysis shows that the boron film is amorphous. It was found that when a boron film is deposited on the surface of steel, a multilayer nanocrystalline structure is formed: actually boron film, thin interlayer located at the interface of the «film (B)/substrate (steel)» system and containing nano-sized iron and chromium borides of FeB, Fe$_2$B, CrB$_6$ composition, adjacent to this interlayer, a transition layer formed by nano-sized grains and subgrains of a solid solution based on γ-iron, containing iron and chromium borides of Fe$_3$B, Fe$_{23}$B$_6$ and Cr$_2$B composition, and a layer of thermodiffusion conversion of steel containing nano-sized particles of iron and chromium borides. It is shown that the hardness of the «film (B)/substrate (AISI 304 steel)» system at a load on an indenter of 1 mN exceeds the hardness of the initial steel at a given load on the indenter by 2.2 times. The hardness of the «film (B)/substrate (AISI 310S steel)» system exceeds the hardness of the initial steel by 1.2 times. The «film (B/W)/substrate (steel)» system was formed and its high-speed melting with an intense pulsed electron beam was carried out. The formation of a columnar structure containing particles of borides and carborobides of iron and chromium was revealed. It is shown that the hardness of the «film (B/W)/substrate (AISI 304 steel)» system after irradiation with an electron beam is 1.5 times lower than the hardness of the AISI 304 steel in the initial state. The hardness of the «film (B/W)/substrate (AISI 310S steel)» system irradiated with a pulsed electron beam is 2.3 times lower than the hardness of the AISI 310S steel in the initial state.
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