Combined electron-ion-plasma boriding of high-chrome austenitic steel

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Abstract. A combined modification of the surface of high-chromium stainless steel 12Cr18Ni10Ti was carried out, including electro-explosive alloying with titanium and boron and subsequent irradiation with an intense pulsed electron beam. The formation of a multiphase submicro-nanocrystalline surface layer with a thickness of up to 70 μm was revealed. It was shown that the concentration of boron in the surface layer varies nonmonotonically, reaching a maximum value (≈19 at.%) at a distance of (10-15) μm from the alloying surface. It was established that the hardness and wear resistance of the modified steel layer exceeds the hardness of the initial state by 7 times, wear resistance - more than 9 times.

Keywords: electron beams, irradiation, steel, structure, elemental composition.

1. Introduction
Boriding is a promising method for the chemical-thermal treatment of metals and alloys [1, 2]. Boron saturation in gaseous, liquid, and solid media are the most common methods in terms of industrial applications [1, 2]. Thermocyclic boriding [3], electron-beam boriding [4] and boriding using laser beams methods are at the development stage [5]. This boriding method by its mechanism is a modification of the boriding method from solid-phase saturating lubricant during chemical-thermal treatment [6]. The most uniform and uniform penetration of boron into the surface layer of the metal is realized using the gas boriding method; however, the boriding gas mixtures that are used are often explosive, what limits the application of this technique. The limited boriding use in powders and pastes is due to the high complexity and high cost of the processes, the difficulty of forming a certain structure and phase composition of the hardened layer and the properties of the core. Constraining factors for the widespread use in industry of existing boriding techniques are also the process duration (tens of hours), high temperature (1000–1200 0C) and a low level of process environmental friendliness.

In recent decades, new methods of hardening and protecting the materials surface based on the use of concentrated energy fluxes have been developed: pulsed plasma flows [7], in particular, electroexplosive alloying (EVL) and electroexplosive deposition (EVN) coatings [8]. Their essence lies in the formation of the necessary structural-phase states and properties of surface layers by treating metals and alloys with plasma flows of an electrical explosion of conductor’s products. The additional treatment of the alloyed layer with high-intensity pulsed electron beams is a promising direction for the development of the electroexplosive alloying method [9].
The aim of this work is to analyze the structural-phase transformations of the surface layer of stainless steel that take place under combined exposure, including electroexplosive alloying with titanium and boron and subsequent irradiation with an intense pulsed electron beam.

2. Material and method

The material under study was stainless steel grade 12Cr18Ni10Ti (GOST 5632-72), having the following chemical composition (wt.%): up to 0.12 C - (17-18) Cr - (9-11) Ni - 0.8 Ti - up to 2 Mn - up to 0.8 Si - up to 0.3 Cu - up to 0.02 S - up to 0.036 P (Fe - the rest). The samples had the form of plates measuring 10 x 10 x 5 mm. At the first stage, the surface treatment of steel was carried out by electroexplosive alloying on an electro explosive setup EVU 60/10 [8]. As an electrically conductive material, a foil of technically pure titanium VT1-0 grade was used. A portion of boron powder was located on a titanium foil.

Amorphous boron powder was used (B-99V-TU 1-92-1549, B > 99%, particle diameter (0.5-5) microns. Parameters of electric explosive alloying: exposure power density 2.2 GW/m²; exposure pulse duration 100 μs; the mass of titanium foil is 423.7 mg; the mass of boron powder is 75 mg. In the second stage, the modified steel surface was treated with a low-energy intense pulsed electron beam [10] with the following parameters: electron beam energy density of 40 J/cm² and 20 J/cm², pulse duration of electron beam exposure 200 μs and 50 μs, quantity pulse number 3. The choice of the irradiation mode was based on the results of modeling the temperature field [11].

The study of the steel structure in the initial state and after modification was carried out by optical (Microvisor metallographic µVizo-MET-221), scanning (Philips SEM 515) and transmission diffraction (JEM-2100F) electron microscopy. Analysis of the elemental composition of the samples was carried out by X-ray spectral microanalysis. The properties of the modified layer were characterized by determining microhardness (PMT-3 device, 1 N indenter load) and wear resistance (TRIBotechnik device; dry friction condition at room temperature, counterbody – 100Cr6 ball with a diameter of 6 mm, track diameter 4 mm, sample rotation speed 2, 5 cm/s, indenter load 10 N, number of revolutions 8000). The wear resistance of the surface layer of the material was calculated after profilometry of the formed track.

3. Results and discussion

The material under study, before modification, was a polycrystalline aggregate with an average grain size of 19.6 μm (the real grain size varied from 1.0 μm to 86.4 μm). Microtwins (Figure 1a) and a dislocation substructure in the form of randomly distributed dislocations and dislocation grids (Figure 1b) are present in the volume of grains of the initial steel. The scalar dislocation density is $4.8 \times 10^{10}$ cm². The phase composition of the steel is characterized by the presence of chromium carbide particles of the M23C6 type, the average size of which is 167 nm.

![Figure 1](image-url). The structure of steel 12X18H10T in the initial (before modification) state.
Electroexplosive alloying of the steel surface is accompanied by the formation of a rough surface containing microdrops, microcraters and microcracks (Figure 2a). Subsequent irradiation of the modified surface with an intense pulsed electron beam leads to melting of the surface layer with a thickness of up to 30 μm and a significant smoothing of the relief (Figure 2b).

**Figure 2.** The surface structure of steel 12Cr18Ni10Ti after electroexplosive alloying (a) and additional irradiation with an intense pulsed electron beam (b).

The elemental and phase composition, the state of the defective substructure of the modified steel layer was studied by transmission electron diffraction microscopy. Foils were prepared by ion thinning methods from plates cut perpendicular to the surface of modification. This arrangement of the foil made it possible to analyze the state of the material at various controlled distances from the surface of the modification. As a result of the studies, it was found that combined treatment, including electroexplosive alloying and electron beam irradiation, leads to surface layer with a thickness up to 70 μm modification. A typical image of the steel structure at the different distances from the modified surface is shown in figure 3. It is clearly seen that the modified layer has a submicro-nanocrystalline structure and contains a large number of inclusions of the second phase. Inclusions have a diverse shape, ranging from spherical to cubic. The sizes of inclusions vary from tens to hundreds of nanometers.

**Figure 3.** An electron microscopic image of the structure of 12Cr18Ni10T steel after combined treatment including electro-explosive alloying and subsequent irradiation with an intense pulsed electron beam; a - layer located at a depth of 5 μm; b - a layer located at a depth of 45 microns.

The elemental composition of the modified layer was determined by X-ray microanalysis of thin foil [12]. A typical image of the energy spectra obtained from a sample site located at a distance of 40 μm from the surface of the modified layer is shown in figure 4. An analysis of the results presented in this
Figure and in table 1 indicates that combined treatment is accompanied by alloying of 12Cr18Ni10Ti steel with boron and titanium atoms. The presence of boron atoms is detected in a layer up to 70 μm thick. The farther from the surface of the sample, the presence of boron atoms is not detected. The concentration of boron atoms in the alloyed layer varies nonmonotonically and reaches a maximum value at a distance of (10-15) microns from the alloying surface, amounting to ≈19 at.%.

![Energy spectra](image)

**Figure 4.** Energy spectra (a) of 12Cr18Ni10Ti steel subjected to combined processing, obtained from the foil section (b), located at a depth of 50 μm.

**Table 1** The results of a quantitative analysis of the elemental composition of the foil plot shown in figure 4b.

| Element | (keV) | Mass. % | Error, % | Atom. % |
|---------|-------|---------|----------|---------|
| B (Kα)  | 0.183 | 1.61    | 0.04     | 7.49    |
| Ti (Kα) | 4.508 | 23.97   | 0.00     | 25.14   |
| Cr (Kα) | 5.411 | 12.91   | 0.01     | 12.47   |
| Fe (Kα) | 6.398 | 51.71   | 0.00     | 46.52   |
| Ni (Kα) | 7.471 | 9.79    | 0.02     | 8.38    |

The phase composition of the doped layer was studied by electron diffraction microscopy of thin foils by indicating microelectron diffraction patterns and using the dark-field analysis method [13-15]. The studies performed revealed the presence of the following phases in the modified layer: a solid solution based on γ-iron (alloyed austenite), titanium, chromium and iron borides, titanium carborides. In figure 5 shows an example of a phase analysis of a modified steel layer performed by diffraction electron microscopy, showing the presence of the γ phase (iron-based solid solution, fcc crystal lattice), titanium borides of the composition Ti₂B₃ and TiB in the selected foil section.

The mechanical and tribological tests of steel 12Cr18Ni10Ti, modified by the integrated method, were performed. It has been established that the hardness and wear resistance of steel after modification reaches values exceeding the initial state hardness by 7 times, and wear resistance by more than 9 times. The friction coefficient of modified steel is close to the coefficient of friction of steel in the initial state.
Figure 5. TEM structure of 12Cr18Ni10Ti steel after combined treatment including electro-explosive alloying and subsequent irradiation with an intense pulsed electron beam; a, b - bright field; c – micro-electron diffraction pattern obtained from the foil section (b) limited by the selector diaphragm; d-f dark fields obtained in reflections of [002] γ-Fe, [101] Ti2B5, [220] TiB; on (c) the arrows indicate the reflections in which the dark fields are obtained: d - reflex 1, e - reflex 2, f - reflex 3. The layer located at a depth of 25 μm is analyzed.

4. Conclusion
It has been shown by X-ray diffraction analysis methods that the alloying and impurity elements of cast silumin are in a localized state and form inclusions of micron sizes of different chemical composition. The irradiation of silumin with an intense pulsed electron beam makes it possible to form a submicron structure of high-speed crystallization of a cellular type in the surface layer up to 100 microns thick. Inclusions of the cast state of silumin are not detected in this surface layer. The formation of cells of two morphologically different types was revealed. Firstly, the cells, which
volume is predominantly enriched with aluminum atoms, separated by layers of nanoscale thickness enriched with silicon, nickel, copper, and iron atoms. Secondly, the cells of the nanoscale lamellar eutectic of Al-Si system. The cells of this type are also separated by layers enriched with silicon, nickel, copper, and iron atoms. It is important to note that inclusions of the second phase (silicon and intermetallic compounds), which form the structure of the surface layer, are nanoscale and, undoubtedly, will contribute to plasticization of silumin.

A combined modification of the surface of high-chromium stainless steel 12Cr18Ni10Ti was carried out, including electro-explosive alloying with titanium and boron and subsequent irradiation with an intense pulsed electron beam. The formation of a multiphase submicro-nanocrystalline surface layer with a thickness of up to 70 μm was revealed. It was shown that the concentration of boron in the surface layer varies nonmonotonically, reaching a maximum value (≈19 at.%) at a distance of (10-15) μm from the alloying surface. It was established that the hardness and wear resistance of the modified steel layer exceeds the hardness of the initial state by 7 times, wear resistance - more than 9 times.

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