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# Effect of electron-beam treatment on the structure and properties of (B + Cr) film deposited on a high-entropy alloy AlCrFeCoNi

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A R T I C L E I N F O

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A B S T R A C T

The B + Cr film with a thickness of ~ 1 μm was deposited by plasma-assisted RF sputtering on AlCrFeCoNi HEA of non-equiatomic composition prepared by WAAM. The subsequent treatment included electron beam irradiation of the surface with parameters as follows: energy density $E_s$=(20–40) J/cm$^2$, pulse duration 200 μs, frequency 0.3 s$^{-1}$, number of pulses 3. It has been proved that microhardness increases by 2 times and wear resistance – by 5 times, whereas friction coefficient decreases by 1.3 times at an energy density Es = 20 J/cm$^2$. High-speed crystallization of the surface layer leads to the formation of a cellular structure with cell sizes (150–200) nm. The increase in strength and tribological properties effected by electron beam treatment has been interpreted with the three factors in view: (1) the decreasing cell size, (2) formation of chromium and aluminum oxyborides, (3) formation of a HEA crystal lattice incorporating solid solution of boron.

## 1. Introduction

During the last decade, studies of high-entropy alloys (HEAs) with equal or close concentration of components have been of primary importance in modern physics' materials science [1,2]. This is due to the high functional properties of HEAs. Methods for obtaining HEAs are being rapidly developed and improved: crystallization from melts after argon-arc, induction, selective laser melting [3–6]. Methods for producing HEAs in the form of thin coatings and films make up a separate group. Usually they are based on the use of magnetron sputtering to obtain multicomponent nitrides [7,8], carbides [9], oxides [10]. In recent years, this method has been used to obtain multilayer nanostructures in which HEA layers alternate with layers of pure metal [11,12]. High-entropy coatings and films instead of bulk HEAs reduce the cost of products and expand their application areas. Coatings from FeCoNiCrX (X = Mn, Al) HEA on a copper substrate, obtained by electrodeposition, significantly increase the microhardness, corrosion resistance and reduce the friction coefficient and wear [13].

In order to improve the surface properties of HEAs, they are subjected to various types of surface treatment: electrolytic polishing, electrical discharge machining, milling, grinding, mechanical polishing; combination of these methods is also applied [14] – thermochemical surface treatment using carbon, nitrogen or boron. Higher hardness values can be achieved by boriding compared to carburizing and nitriding, and it is predicted that boronizing can give more promising results in HEAs processing, since the chemical elements Fe, Co, Cr, Ni present in HEAs have a high tendency to form metal borides [15–18]. The main method of HEAs boriding is currently boriding by powder metallurgical techniques.

One of the promising and highly efficient methods of surface modification is pulsed electron beam treatment [19]. It provides ultrahigh rates of surface heating (up to $10^8$ K/s) and cooling due to heat removal to the bulk of the material, resulting in the formation of nonequilibrium submicro- and nanocrystalline structural-phase states.

The main advantages of pulsed electron beam irradiation, compared with traditional laser irradiation, include a significantly higher efficiency (up to 90 %) of electronic sources, high efficiency of energy input into the surface layer of the material (low electron reflection coefficient), the possibility to control all the parameters of irradiation with a high degree of energy localization in the surface layer, a significantly large (up to 10 cm$^2$) surface area processed per pulse.

The purpose of this work is to establish the patterns of evolution of the elemental and phase composition, defect substructure and properties of the "(B + Cr) film / (AlCrFeCoNi HEA) substrate" system irradiated

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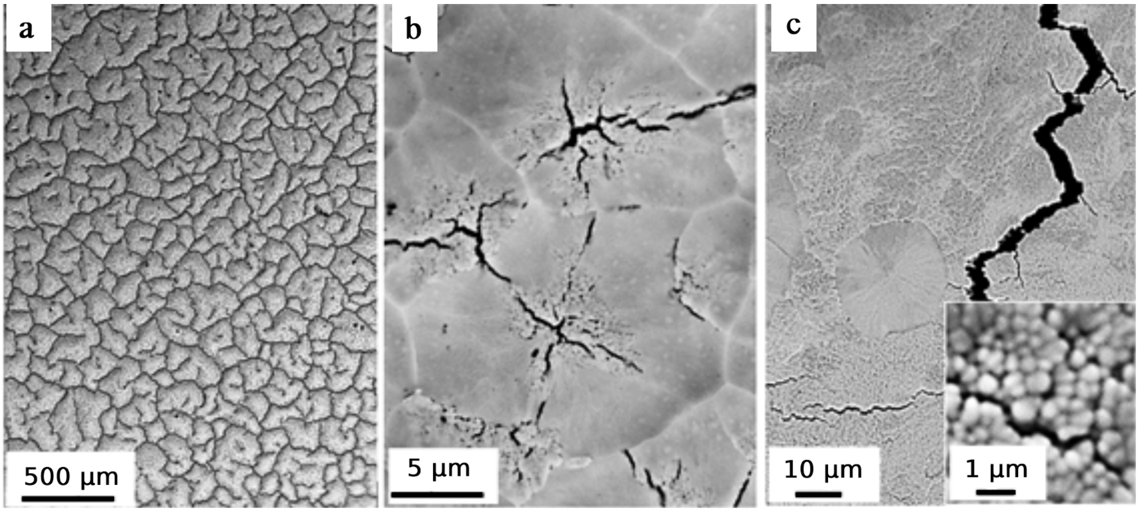


**Fig. 1.** Electron microscopic image of the structure of "film/substrate" system irradiated with a pulsed electron beam at $E_s$ (J/cm$^2$) equalling to 20 (a), 30 (b), and 40 (c).

with a pulsed electron beam.

## 2. Materials and methods

A high-entropy alloy (HEA) of a non-equiatomic composition AlCrFeCoNi obtained by the additive technology WAAM – wire-arc additive manufacturing was used as a research material. Initially, a B + Cr film was formed on the HEA surface with the thickness of each element – 0.5 μm. The formation of a boron film on the HEA samples surface was carried out by plasma-assisted high-frequency cathode sputtering from boron powder with the following process parameters: power W = 800 W, frequency f = 13.56 MHz, duration of processes t = 35 min. A chromium film of 0.5 μm thickness was deposited on the samples with a boron film for 10 min. Next, the film formed on the substrate was irradiated with a pulsed electron beam with the following parameters: energy of accelerated electrons 18 keV, energy density of the electron beam (20–40) J/cm$^2$, pulse duration 200 μs, number of pulses 3, pulse repetition rate 0.3 s$^{-1}$, working gas pressure (argon) 0.02 Pa. Under such irradiation, the HEA surface temperature exceeds the melting point. With high-speed heating and subsequent cooling at a rate of ~10$^7$ K/s, it is possible to form a submicro- and nanocrystalline multiphase structure containing borides as a strengthening phase.

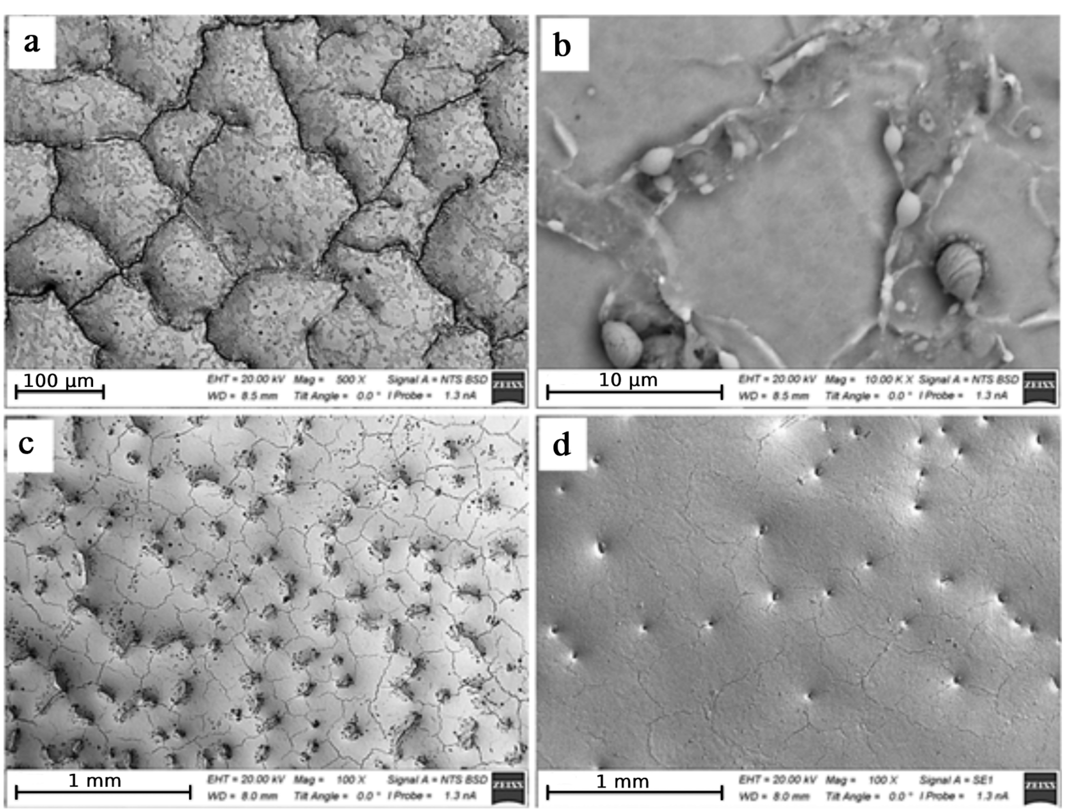


**Fig. 2.** Electron microscopic image of the structure of "film/substrate" system irradiated with a pulsed electron beam at $E_s$ (J/cm$^2$) equalling to 20 (a, b), 30 (c), and 40 (d).

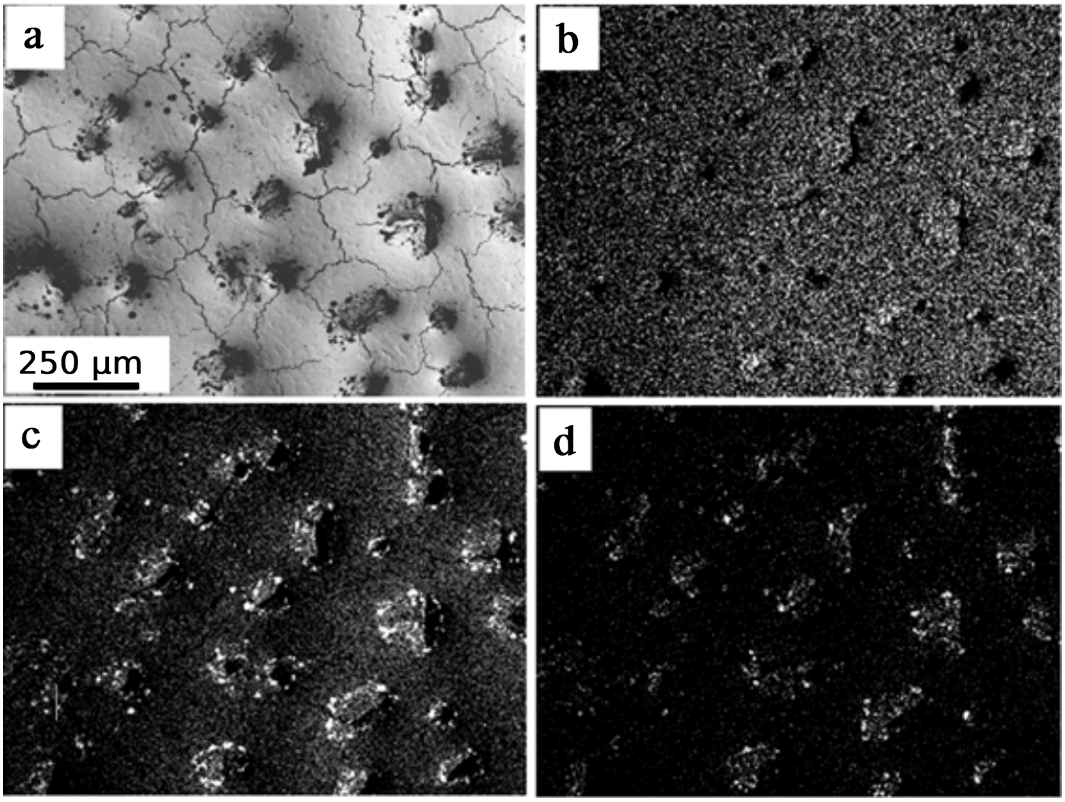


**Fig. 3.** Electron microscopic image of the structure of "film/substrate" system irradiated with a pulsed electron beam at an energy density of $E_s = 30$ J/cm$^2$, b-d - images of the sample area (a), obtained in the characteristic X-ray radiation of Cr (b); O (c); Al (d) atoms.

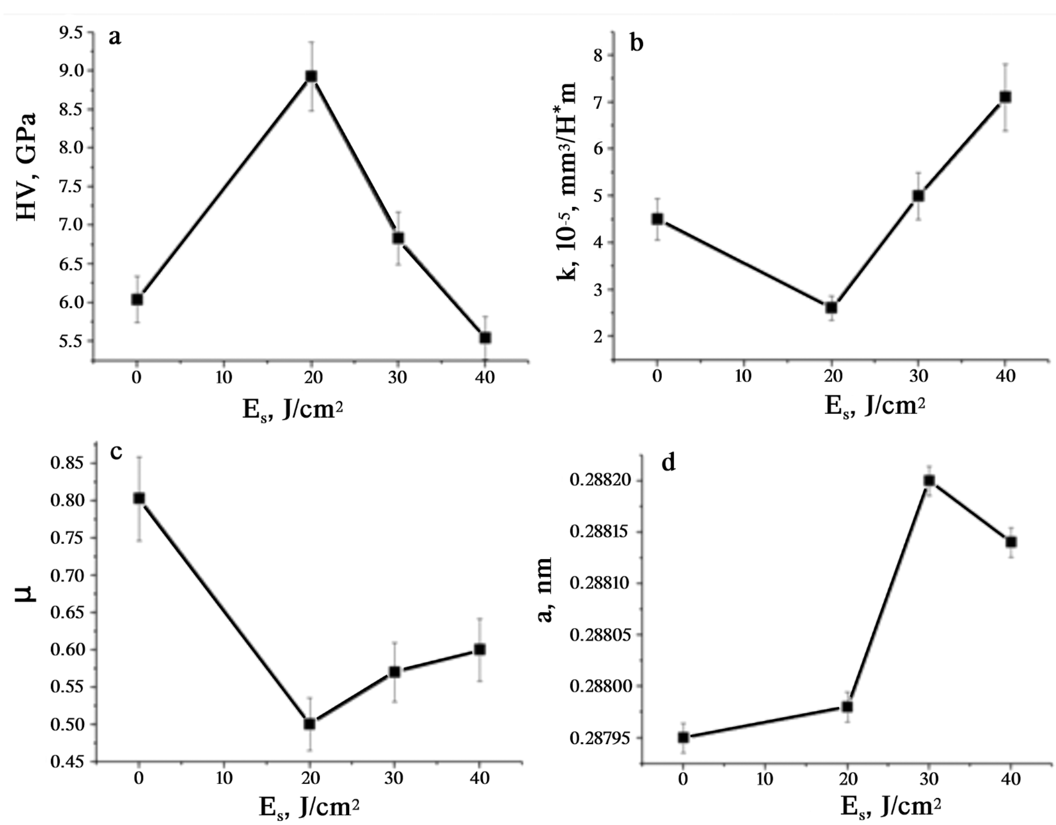


**Fig. 4.** Dependence of microhardness (a), wear parameter (b), friction coefficient (c) and crystal lattice parameter (d) of the surface layer of the "film/substrate" system on the energy density of the electron beam. The HEA microhardness in the initial state is 4.7 GPa, the wear parameter is $14{*}10^{-5}$ mm$^3$/N*m, the friction coefficient is 0.65.

Investigations of the elemental and phase composition, the state of the defective substructure of the "film (Cr + B) / (HEA) substrate" system were carried out by scanning electron microscopy (SEM 515 Philips device with an X-ray microprobe analyzer EDAX ECON IV). The phase composition and the state of the crystal lattice of the main phases of the surface layer of the samples were studied by the methods of X-ray phase and X-ray diffraction analysis. The phase composition was analyzed using the PDF 4+ databases, as well as the POWDER CELL 2.4 full-profile analysis program. The hardness of the material was determined according to the Vickers scheme on a PMT-3 microhardness tester at a load of 0.5 N. The study of the tribological (friction coefficient and wear parameter) characteristics of the material was carried out on a Pin-on-Disc and Oscillating TRIBOtester (TRIBOtechnic, France).

## 3. Results and discussion

The HEA formed by WAAM has a polycrystalline structure with an average grain size of 12.3 μm. According to X-ray microanalysis, the ratio of elements is as follows (at. %) 33.4 Al; 8.3Cr; 17.1 Fe; 5.4Co; 35.7 Ni. Using mapping methods, it was found that Co atoms are uniformly distributed in the volume of the alloy, the boundaries of grains and dendrites are enriched with Cr and Fe atoms, and the volume of grains is enriched with Al and Ni atoms. According to the results of X-ray phase analysis, the studied HEA has a simple cubic lattice with a parameter of 0.28795 nm.

Irradiation of the "film/substrate" system is accompanied by fragmentation of the sample surface layer with a network of microcracks (Fig. 1). This indicates a high level of tensile stresses in the HEA surface layer during irradiation. The average fragment size increases with $E_s$ growth from 160 μm ($E_s$ = 20 J/cm$^2$) to 270 μm ($E_s$ = 40 J/cm$^2$). At the same time, a decrease in the average grain size by 4.5 times is observed at $E_s$ = 20 J/cm$^2$ compared to the size before irradiation.

A structure of high-speed cellular crystallization is formed (Fig. 1, b, c) in the volume of grains at $E_s$ = (30 and 40) J/cm$^2$. This indicates the melting of the samples surface layer in this irradiation mode. At $E_s$ = 30 J/cm$^2$, the surface temperature can reach ~2100 K [20]. At $E_s$ = 30 J/cm$^2$, cells are formed at the junctions of fragment boundaries (Fig. 1, b); at $E_s$ = 40 J/cm$^2$, cells are formed over the entire sample surface (Fig. 1, c). The cell size weakly depends on the energy density of the electron beam and is (150–200) nm.

Irradiation of the "film/substrate" system is accompanied by the destruction (dissolution) of the deposited film. A "network" structure is formed on the HEA surface at $E_s$ = 20 J/cm$^2$, in which the film of (2–9) μm thickness is interlayered along the boundaries of the network cells, the dimensions of which vary within (5–25) μm (Fig. 2, a, b). The presence of globular formations in the interlayers (Fig. 2b) indicates the film melting and, consequently, liquid-phase alloying of the HEA surface layer with chemical elements of the (Cr + B) film, as well as the formation of chromium borides. An island structure is formed on the HEA surface at $E_s$ = 30 J/cm$^2$ (Fig. 2, c). The size of the islands is (50–80) μm. The island sizes decrease to (25–40) μm at $E_s$ = 40 J/cm$^2$, and their number per unit area of the sample surface decreases (Fig. 2, d). X-ray microanalysis (mapping method) showed that these islands are enriched with chromium, aluminum and oxygen atoms (Fig. 3).

The pulsed electron beam treatment of the "film/substrate" system leads to an increase in the microhardness, a decrease in the wear parameter and friction coefficient (Fig. 4, a-c), reaching its maximum at the energy density of electron beam $E_s$ = 20 J/cm$^2$. This is due, first, to a 4.5-fold decrease (relative to the original HEA) in the average grain size of the HEA surface layer. Secondly, due to the formation of a network-type structure, strengthened, possibly, by chromium borides. Thirdly, by alloying the HEA surface layer with boron atoms to form an interstitial solid solution. This is evidenced by an increase in the crystal lattice parameter of the alloy irradiated with a pulsed electron beam (Fig. 4, d).

## 4. Conclusion

The elemental and phase composition, defective substructure, mechanical and tribological properties of the surface of a B + Cr film deposited on a HEA and irradiated with a pulsed electron beam were analyzed using the methods of modern physical materials science.

The irradiation mode was determined (energy density 20 J/cm$^2$, duration 200 μs, number of pulses 3, frequency 0.3 s$^{-1}$) improving the "film/substrate" system parameters. Possible reasons for the increase in the strength and tribological properties of the system were discussed, which include the decrease in the average grain size, formation of particles of Cr and Al borides and oxyborides, and the incorporation of boron atoms into the HEA lattice.

The results obtained in this work can be used in the formation of surface layers of materials operating in friction pairs, especially since in the amorphous state, boron can act as a solid heat-resistant lubricant to reduce the friction coefficient. We also note that the electron-ion-plasma boriding method used in the work is characterized by environmental cleanliness and production safety, is aimed at minimizing resource and energy costs and obtaining high functional characteristics of the final product.

## CRediT authorship contribution statement

**Yurii Ivanov:** Methodology, Investigation. **Victor Gromov:** Conceptualization, Supervision, Writing – review & editing. **Sergey Konovalov:** Supervision, Writing – original draft. **Michail Efimov:** Formal analysis. **Yulia Shliarova:** Formal analysis, Writing – original draft. **Irina Panchenko:** Formal analysis, Writing – original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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