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Evolution of structure of AlCoCrFeNi high-entropy alloy on irradiation by pulsed electron beam

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By the methods of modern physical materials science the change in structural-phase state of AlCoCrFeNi high-entropy alloy (HEA) of nonequiatomic composition obtained by the methods of wire arc additive technology (WAAM) after irradiation by electron beams with energy density of $10-30\,\mathrm{J/cm^2}$, durality of $50\,\mu\mathrm{s}$, frequency $0.3\,\mathrm{s^{-1}}$ is studied. In the initial state the alloy had a dendritic structure indicating the inhomogeneous distribution of elements. It is shown that electron beam processing forms the structure of high-velocity cellular crystallization with cell size of $100-200\,\mathrm{nm}$, along boundaries of which the nanodimensional ($15-30\,\mathrm{nm}$) inclusions of the second phase enriched in Cr and Fe atoms are located.

Keywords: High-entropy alloy, electron beam processing, structure, phase composition.

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For the last two decades, the researchers in the field of physical material sciences have focused on the study of high entropy alloys (HEA) having unique properties versus conventional doped alloys [1]. High entropy alloys contain 5 and more elements with the content of 5 to 35% [2,3], which must lead to their heterogeneous distribution within the volume.

One of the most promising methods for the HEA production is a new (wire arc additive manufacturing (WAAM)) technology [4]. The AlCoCrFeNi HEA manufactured under this method has a distinctive dendrite structure, which indicates the heterogeneous distribution of doping elements in the ingot volume [5]. A method enabling alloy homogenization is the one based on the sample surface exposure to the low-energy intensive pulsed electron bunch. Superhigh rates (up to $10^9\,\mathrm{K/s}$) of heating of a comparatively thin (dozens–hundreds μm) superficial layer up to the melting temperature and further high-rate crystallization of the melt allow to form a submicro-nanocrystalline structure featuring a high degree of homogeneity of the chemical elements distribution [6,7]. Herein we discussed the impact of the electron bunch energy density on the structural-phase condition of the superficial layer of HEA.

Samples of the AlCoCrFeNi HEA were formed under the wire arc additive manufacturing (WAAM) technology in the Ar atmosphere (99.99%). The alloy contains 36.5 at.% of aluminum, 33.7 at.% of nickel, 16.4 at.% of iron, 8.6 at.% of chromium, and 4.9 at.% of cobalt, i.e. the material obtained should be attributed to the non-equiatomic composition HEA.

Layers application modes not differed from that described in [5]. The samples were subjected to irradiation by the pulsed electron bunch with the following parameters: energy of accelerated electrons 18 keV, density of the electron bunch energy $10-30\,\mathrm{J/cm^2}$, bunch pulse duration $50\,\mu\mathrm{s}$, pulse repetition rate $0.3\,\mathrm{s^{-1}}$, the number of the irradiation pulses is 3, irradiation was done at the residual pressure of inert gas (argon) in the operating chamber of the plant $2\cdot10^{-2}\,\mathrm{Pa}$.

The structure and element composition of the samples were studied by the scanning electron microscopy methods (the LEO EVO 50 and TESCAN VEGA instruments equipped with the INCA Energy energy-dispersive analyzer). A defected substructure and distribution of chemical elements were studied by the transmission electron microscopy methods (the JEOL JEM-2100 instrument) [8]. The studied objects (foils with the thickness of $150-200\,\mathrm{nm}$) for the transmission electron microscope were manufactured by ion etching (Ion Slicer plant (EM-09100IS), argon) of plates cut out from a solid HEA ingot. The structure and element composition was analyzed in the layer with the thickness of $5-10\,\mu\mathrm{m}$, adjacent to the irradiation surface.

HEA irradiation by the pulsed electron bunch with the electron bunch energy density of $E_S = 10\,\mathrm{J/cm^2}$ does not result in the destruction of the dendrite crystallization structure, which is specific for the alloy in original condition [5]. It indicates the absence of melting of the superficial layer of irradiated samples. Liquid-phase transformation of the structure of the superficial layer of HEA is found only

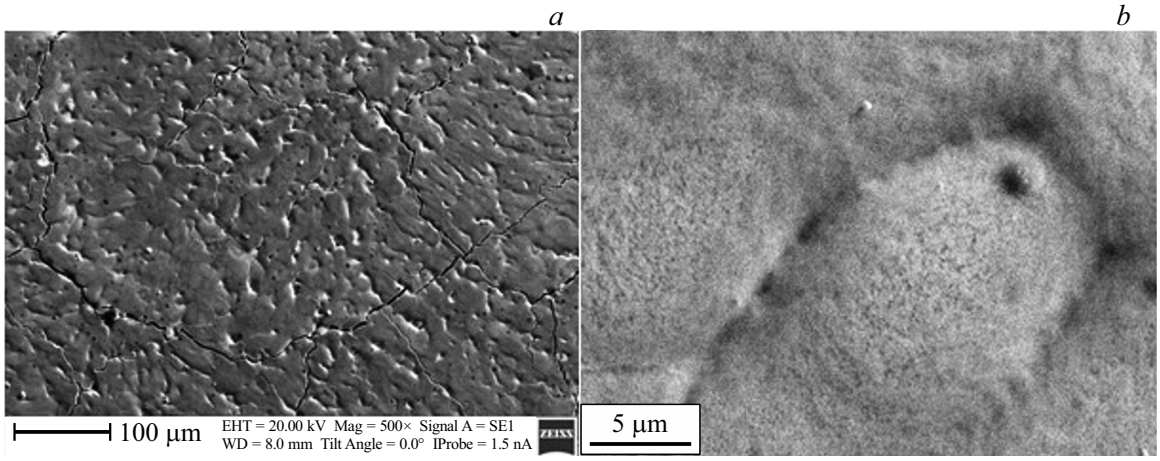

Figure 1. Electron microscope image of the HEA structure formed as a result of exposure to the pulsed electron bunch ($20\,\mathrm{J/cm^2}$).

in the near-to-the-boundary area of the grain (dendrite) structure. High-speed transformation of the structure is accompanied by the formation of interlayers having submicro-nanocrystalline structure with the crystallites size of $100-200\,\mathrm{nm}$.

The studies of the element composition of dendrites and interdendrite spaces of the superficial layer performed by using the methods of electron microprobe analysis have shown that interdendrite spaces are enriched with Al, Ni and Fe chemical elements. The dendrites are enriched mainly by chromium atoms. The cobalt atoms are uniformly distributed within the ingot volume. The most sweating element of the alloy is aluminum (segregation coefficient is $\delta = 9.2$), the least sweating element is cobalt ($\delta = 2.1$).

HEA irradiation by the pulsed electron bunch with the electron bunch energy density of $E_S = 20\,\mathrm{J/cm^2}$ results in the partial destruction of the dendrite crystallization structure (Fig. 1, *a*). It indicates the melting of the superficial layer of irradiated samples. The liquid phase transformation of the structure of the superficial layer of HEA is accompanied by the formation of a nanocrystalline structure within the volume of grains (Fig. 1, *b*).

Analysis of brittle fractures has shown that the superficial layer with the thickness of $\approx 15\,\mu\mathrm{m}$ formed after irradiation has a submicro-nanocrystalline structure. Its thickness rises with the increase of the electron bunch energy density and reaches $\approx 20\,\mu\mathrm{m}$ at $E_S = 30\,\mathrm{J/cm^2}$. A high-rate cellular crystallization structure is formed in it. The volume of crystallization cells is enriched with atoms of aluminum, nickel and iron. The second phase inclusions enriched mainly with the chromium atoms are arranged at the joints and along the cell boundaries. The size of crystallization cells is $100-200\,\mathrm{nm}$; the size of inclusions arranged at the joints of cells is $20-25\,\mathrm{nm}$; of those arranged along the cell boundaries — $10-15\,\mathrm{nm}$.

The studies of element composition of cells of high rate crystallization and the second phase particles (Fig. 2, see table) provide the ground for the conclusion that the high rate crystallization cells (areas of the analysis designated by inscriptions spectrum *1–5*) are enriched with Al and Ni chemical elements. The second phase particles arranged at the boundaries and the joints of crystallization cells (areas of analysis designated by inscriptions spectrum *8–11*) are mainly enriched by Cr and Fe atoms. Atoms of Co are uniformly distributed within the superficial layer volume. The most sweating element of the alloy superficial layer exposed to the pulsed electron bunch ($20\,\mathrm{J/cm^2}$, $50\,\mu\mathrm{s}$, 3 pulses, $0.3\,\mathrm{s^{-1}}$) is Cr (segregation coefficient of $\delta = 5.4$), the least sweating is Co ($\delta = 1.9$). The element composition of the areas of spectra *6, 7, 12* is hard to compare with that of the zones within the volume of cells or at their boundaries. It can be assumed that these zones refer to mixed ones, i.e. partially contain the material of the volume of cells and material of their boundaries.

At the electron bunch energy density of $30\,\mathrm{J/cm^2}$ a superficial layer is also formed, which has the structure of high rate cellular crystallization. The crystallization cells have a round shape. The cell size varies within 100 to 150 nm. The cells are outlined by the second phase interlayers. The interlayer thickness varies within $15-30\,\mathrm{nm}$. The volume of cells is enriched with Al and Ni chemical elements. Mainly the chromium and iron atoms constitute the second phase particles. Cobalt atoms are uniformly distributed within the volume of modified layer.

The most sweating element of the superficial layer of the alloy is Cr (segregation coefficient is $\delta = 10.5$), the least sweating element is Co ($\delta = 1.6$). The generalized results obtained during electron microprobe analysis of HEA in the original condition and after irradiation by the pulsed electron bunch characterizing the degree of heterogeneity of the doping elements distribution in the superficial layer are given in Fig. 3. The most sweating elements of the alloy are chromium and aluminum. The HEA irradiation by the pulsed electron bunch contributes into the alloy homogenization. The highest level of homogeneity of chemical elements distribution in the alloy is reached in case

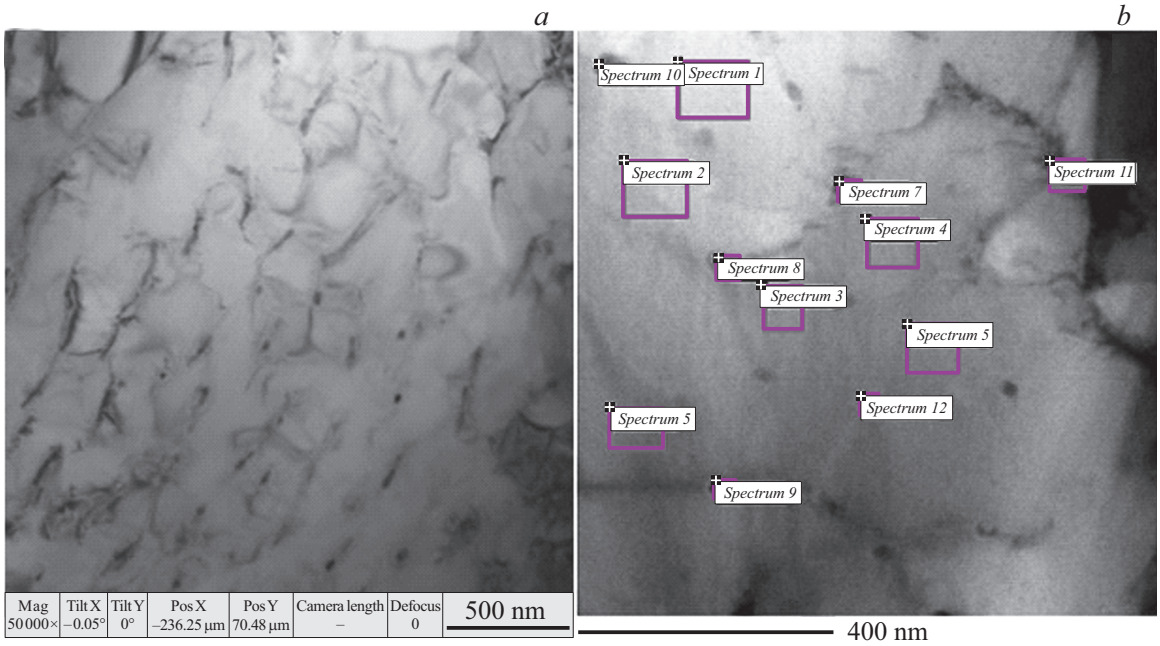

Figure 2. Electron microscope image of a foil area made by TEM (*a*) and STEM (*b*) analysis. The areas of electron microprobe analysis of foil are indicated in (*b*). Irradiation was performed at the density of the electron bunch energy of 20 J/cm^2.

Results of element analysis (at.%) of the foil areas given in Fig. 2, *b*

Spectrum	Al	Cr	Fe	Co	Ni
1	38.9	5.9	10.4	2.9	27.2
2	39.0	5.2	12.5	3.7	25.7
3	36.8	4.3	11.8	4.9	29.7
4	41.3	5.3	11.7	4.7	27.7
5	40.6	5.0	12.0	4.4	29.1
6	38.0	5.0	11.9	3.5	25.4
7	25.2	17.4	14.4	4.0	19.8
8	17.5	23.3	23.5	3.2	12.3
9	24.5	17.5	20.3	5.6	21.5
10	15.8	16.1	21.0	3.8	14.6
11	15.2	21.9	22.4	4.3	20.3
12	28.7	15.7	18.5	4.3	18.8
Average value	30.1	11.9	15.9	4.1	22.7
Maximum value	41.3	23.3	23.5	5.6	29.7
Minimum value	15.2	4.3	10.4	2.9	12.3
δ (max/min)	2.7	5.4	2.3	1.9	2.4

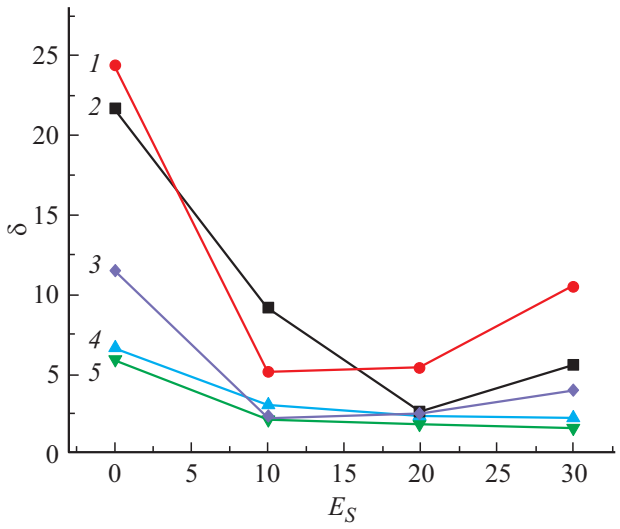

Figure 3. Dependence of the HEA chemical elements distribution heterogeneity coefficient on the electron bunch energy density; *1* — Cr, *2* — Al, *3* — Ni, *4* — Fe, *5* — Co.

of irradiation by the pulsed electron bunch with the electron bunch energy density of 20 J/cm^2.

The HEA irradiation by the pulsed electron bunch results in the formation of the high-rate cellular crystallization structure. The cell size varies within 100 to 200 nm. Nano-size (15–30 nm) inclusions of the second phase enriched with Cr and Fe atoms are arranged along the cell boundaries. It is shown that HEA feature a high degree of heterogeneity of distribution of chemical elements forming the alloy. The most sweating elements of the alloy are chromium and aluminum. The HEA irradiation by the pulsed electron bunch contributes into the alloy homogenization. The irradiation mode was found that allows to form a superficial layer featuring the highest

degree of homogeneity of the chemical elements distribution in the alloy.

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Conflict of interest

The authors declare that they have no conflict of interest.

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