
STRUCTURE, PHASE TRANSFORMATIONS,
AND DIFFUSION

Effect of Aluminum on Fine Structure and Distribution of Chemical Elements in High-Entropy Alloys $\text{Al}_x\text{FeNiCoCuCr}$

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Abstract—Electron-microscopic and X-ray diffraction methods have been used to study the fine structure of cast high-entropy alloys (HEAs) $\text{Al}_x\text{FeNiCoCuCr}$ ($x = 1, 1.5, 1.8$). Disperse precipitates with dimensions of 130–400 and 10–20 nm have been revealed, the character of distribution of which, as well as the amounts, dimensions, and shapes, change with increasing aluminum content. In the equiatomic HEA, copper-containing particles with an fcc structure have been found; in the alloy with $x = 1.8$, particles of bcc Al_4Cu_9 dominate. It has been shown that the most uniform distribution over the matrix is characteristic of Co, unlike other elements, among which Cu and Cr are distributed in the alloy extremely nonuniformly and predominantly enter into the precipitated particles and into clusters in the interparticle spaces, respectively.

Keywords: high-entropy alloy (HEA), structure, distribution of elements, electron microscopy

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INTRODUCTION

The constantly growing needs of modern engineering in materials with high service characteristics gradually leads to the exhaustion of the application of ordinary alloys, including the iron-based alloys. In connection with this, the interest of researchers in studying the so-called high-entropy alloys (HEAs) increased significantly, the specific features of the formation of the crystal lattice, structural hierarchy, phase composition, and mechanical properties of which are insufficiently studied.

Works [1, 2] can be mentioned among the first investigations of HEAs, and they were continued later in [3, 4]. The authors of [1–4] showed the increase in the hardness of the $\text{Al}_x\text{FeNiCoCuCr}$ alloys that is observed with increasing aluminum content, as well as revealed the high thermal stability of these alloys. They have established that, at all hierarchical levels, the size of structural elements in the HEAs, which can change from 7 to 800 nm, is determined to a significant extent by the rate of cooling. The authors also studied the effect of the deviation from the equiatomic composition on the decrease in the concentration of each of the elements ($x = 0.5$) in the AlFeNiCoCuCr HEA, as well as its effect on the phase composition of dendritic and interdendritic regions and their hardness. It has been shown that the decrease in the content of copper to $x = 0.5$ favors the formation of only bcc phase, which leads to a substantial increase in the hardness due to the mechanism of solid-solution hardening.

The phase composition and some features of the structure formation in alloys of a similar system with the content of aluminum varying in the limits of $x = 0–3$ have been studied in both the cast state [2–5] and after rapid cooling by spinning [4, 6, 7]. For the cast alloys, boundary concentrations of Al (x) have been found at which, in the high-temperature region (after the completion of the process of crystallization), transitions occur from the two-phase fcc structure (at $x < 0.6$) to the two-phase fcc + bcc ($0.6 < x < 2.6$), then to the two-phase bcc structure that consists of an ordered matrix and copper-rich phase in the form of particles ($x > 2.6$). According to [2], upon a further decrease in temperature, a spinodal decomposition should occur in the bcc phase, which actively takes place in the temperature range below 700°C and ultimately leads to the modulation of the matrix by particles. The concentration dependence of the crystal-lattice parameters of the fcc and bcc phases was constructed and the increase in these parameters with increasing content of Al was shown. It has been established that the high-temperature phase with the fcc lattice is enriched in copper. In [7], at least six nanosized phases with different morphologies, structure types (A_2 , B_2 , $L1_2$), and chemical compositions were revealed.

After rapid cooling by spinning (with cooling rates of $10^6–10^7$ K/s), in the range of room temperatures, these alloys have only a bcc phase of the B_2 type, which is represented by a homogeneous ultrafine-grained structure modulated with a period of 2 nm at the initial stage of atomic separation. The assumption

Table 1. Chemical composition of the $\text{Al}_x\text{FeNiCoCuCr}$ alloys

Designation of the alloy	Content of aluminum, x	Wt % (at %)					
		Al	Fe	Co	Ni	Cu	Cr
A_1	1	8.8 (17.2)	18.1 (17.1)	18.3 (16.3)	18.9 (16.9)	19.7 (16.3)	16.0 (16.2)
A_2	1.5	12.2 (23.0)	17.4 (15.9)	17.3 (14.9)	18.6 (16.1)	19.4 (15.5)	14.9 (14.6)
A_3	1.8	14.9 (27.3)	16.8 (14.9)	17.1 (14.4)	17.7 (14.8)	18.7 (14.6)	14.7 (14.0)

was made that the modulation occurs along the boundaries of the antiphase domains [7].

Thus, no single viewpoint relative to the phase composition, structure formation, and distribution of chemical elements in the HEAs of the $\text{Al}_x\text{FeNiCoCuCr}$ system, in particular in the cast state, has been established to date, which requires further investigations to be performed in this direction.

Therefore, this work is devoted to investigating specific features of the formation of the fine structure in cast alloys of the $\text{Al}_x\text{FeNiCoCuCr}$ system and the distribution of chemical elements over the phase components in the case of equiatomic composition ($x = 1$) and upon deviations from this composition toward an increased content of aluminum.

EXPERIMENTAL

In this work, we performed a transmission electron-microscopic study of thin foils of three alloys (A_1 , A_2 , A_3) in the as-cast state, the chemical composition of which is given in Table 1 according to the results of spectral analysis.

The alloys were melted in a vacuum arc furnace with the subsequent solidification of the ingot on a water-cooled copper hearth. The mass of the ingots was 30 g. They had the shape of small bars with dimensions of $15 \times 10 \times 40$ mm. The X-ray diffraction analysis was performed using a DRON-3M diffractometer in $\text{Co } K\alpha$ radiation. Electron-microscopic investigations (JEM-2000FX) were carried out using the opportunities of the energy-dispersive analyzer of the LINK system in the transmission mode with the quantitative and qualitative determination of the character of the distribution of elements over the phases.

The samples for the electron-microscopic investigations were prepared according to the traditional scheme with the use of mechanical treatment, i.e., cutting, etching in an electrolyte (of composition 75 g of chromic anhydride CrO_3 , 133 mL of the glacial acetic acid, and 10–20 mL of water), and subsequent polishing of the wafers in an argon plasma using a GATAN-2 instrument. The structures were studied on samples cut in transverse sections of the ingots.

RESULTS AND DISCUSSION

The results of investigation of the formation of the fine structure of as-cast alloys A_1 – A_3 using transmission electron microscopy are given in Fig. 1. An analysis of the investigations performed in [8] indicates that the internal structure of the alloys can be represented by three components, i.e., the matrix phase, which has a bcc lattice, and two types of precipitates of different morphologies. The coarser precipitates have

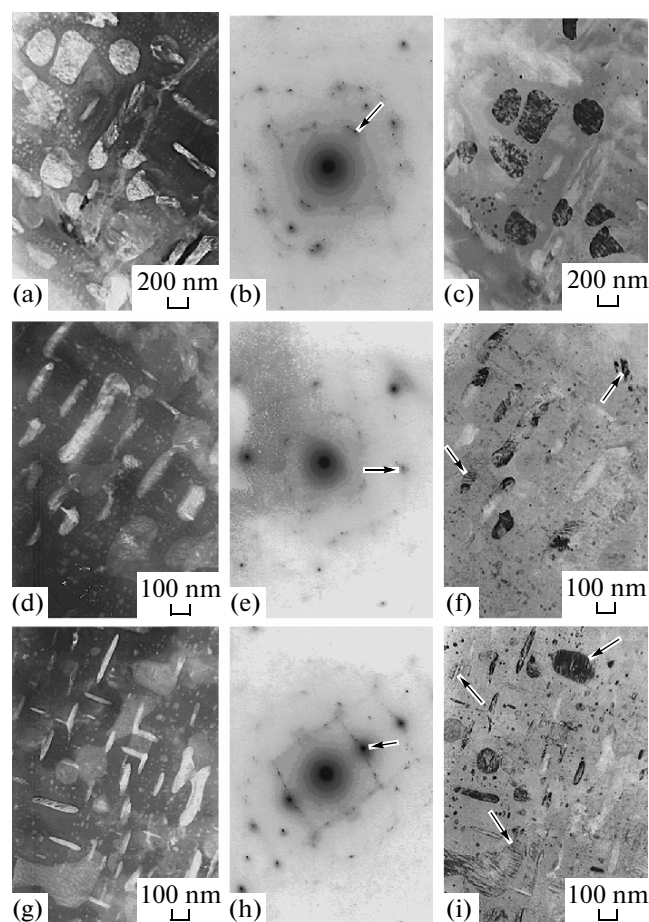


Fig. 1. (a, d, g) Electron-microscopic images of the microstructures of alloys A_1 , A_2 , and A_3 , (b, e, h) electron-diffraction patterns, and (c, f, i) dark-field images taken in the reflections indicated by arrows in b, e, h, respectively. (a–c) Alloy A_1 ; (d–f) alloy A_2 ; (g–i) alloy A_3 .

a globular morphology and an fcc crystal lattice at an increased content of Cu. The changes in their distribution and dimensional parameters (to 5 μm) have been studied using scanning electron microscopy. The sites where they are predominantly located are related to the boundaries of structure elements (interdendritic spaces, grain boundaries), although with increasing concentration of Al in the alloys, these particles of globular shape are encountered fairly frequently in the middle of the coarsest elements of the structure of the matrix phase.

In turn, the matrix phase also contains disperse particles, mainly thin (40–50 nm) platelet precipitates of various shapes (circular, rectangular, and triangular). The dimensions of these precipitates vary from 130 to 400 nm (Fig. 1) and are united into a system of particles oriented at an angle of 90° relative to each other. The planes in which they are located are close to the (120) planes of the bcc matrix. In addition to these precipitates, more disperse particles of globular or slightly elongated shapes are also present in the matrix. Their sizes (diameters) lie in the range of 10–20 nm. These particles apparently have the same origin and are shining in the same reflections as the coarser (platelet) particles do, which follows from the results of their dark-field studies (Figs. 1c, 1f, 1i). Note that, with increasing aluminum concentration (from $x = 1$ to $x = 1.8$) in alloys A_1 – A_3 , the size, density, and uniformity of distribution of both platelet and disperse precipitates become more uniform (Fig. 1).

An analysis of the electron-diffraction patterns indicates a fairly high level of elastic stresses in the lattice. This follows from the significant smearing of the reflections of the matrix phase, which is observed at the minimum density (less than $5 \times 10^8 \text{ cm}^{-2}$) of linear defects (dislocations), which are barely detected in the investigations. This is observed against a background of increasing the hardness and microhardness of the alloys with increasing aluminum content [8], which agrees with the results of measurements of hardness in [9]. Note also the state of the boundaries between the platelet particles and the matrix. No contrast is observed along these boundaries to indicate the presence of defects caused by the violation of their coherency with the matrix. This can be explained by the occurrence of a continuous process of diffusional displacement (in the direction of the growing particles) of atoms of elements that form these particles as a result of a decrease in the solubility of these elements in the solid solution upon a decrease in temperature [10]. The dark-field investigations indicate the absence of fragmentation of the matrix phase, as well as the significant fragmentation of the coarser platelet precipitates (Figs. 1c, 1f, 1i). With increasing aluminum concentration in the alloys, this process leads to the appearance of structure elements of platelet shape

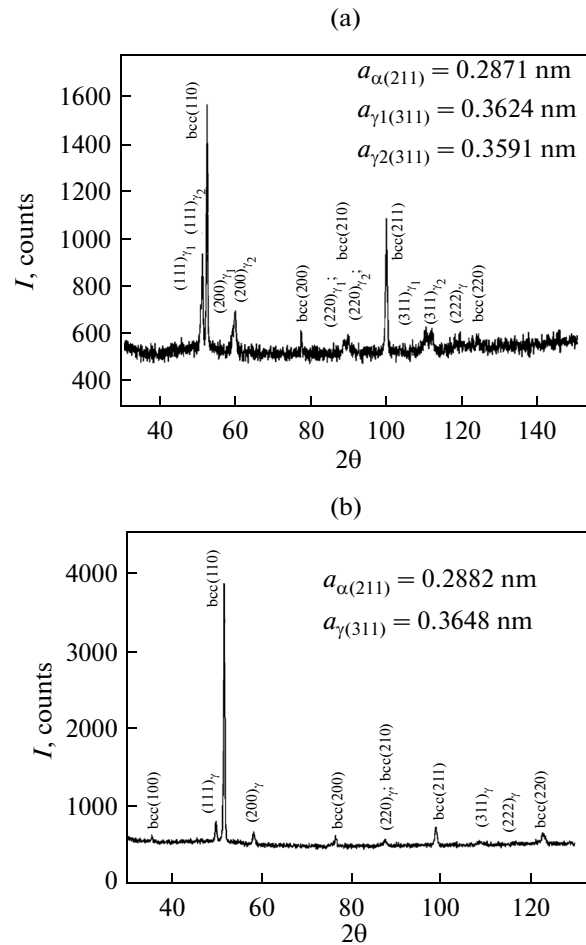


Fig. 2. Results of the X-ray diffraction analysis of the alloys (a) A_1 and (b) A_3 .

(resembling twins) inside the formed particles (Figs. 1f, 1i, sites indicated by arrows).

The above circumstance can be related to the relaxation of the high level of stresses existing at interphase boundaries, which can occur via twinning inside the copper-containing particles. The more disperse precipitates are most likely traceable to the continuation of the decomposition of the matrix phase at low temperatures, especially if we take into account that this decomposition is achieved in limited volumes and under the conditions of the possible escape (displacement) of Cu and Al atoms from the solid solution in view of the continuing decrease in their solubility with decreasing temperature.

The results of X-ray diffraction investigations indicate that the phase composition of the alloys with increasing aluminum concentration changes from three phases (bcc and two fcc phases) to two phases (bcc and fcc) (Fig. 2).

The identification of particles performed via the analysis of electron-diffraction and X-ray diffraction

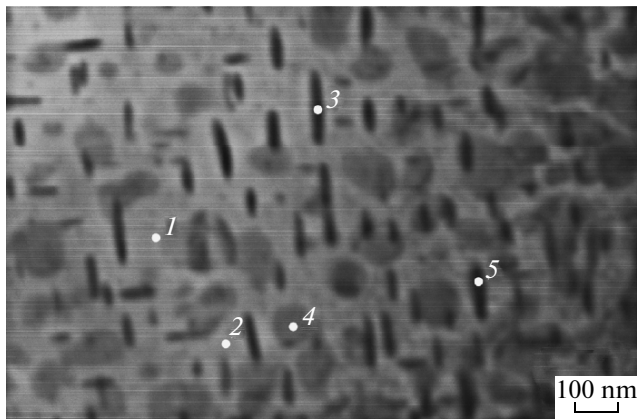


Fig. 3. TEM microstructure of the alloy A_3 . 1–5 indicate the sites where the spectra were registered and quantitative amounts of the elements were determined (Table 2).

patterns indicates the presence of a rather large number of reflections and XRD lines that show that the composition and type of lattice of the particles may be different. In this case, the matrix phase of the alloys A_1 – A_3 can represent a solid solution with a bcc lattice with an increase in the lattice parameter from 0.2871 to 0.2882 nm with increasing aluminum content. The second phase in the alloy A_1 is presented by two types of particles with an fcc lattice and lattice parameters 0.3624 and 0.3591 nm, which are transformed with increasing aluminum concentration into bcc particles of the Al_4Cu_9 type and into some amount of fcc particles with the lattice parameter $a = 0.3648$ nm. At the same time, the presence of additional reflections in the electron-diffraction patterns indicates the possible formation of a more complex set of particles. A comparative analysis of the results of the electron-microscopic and X-ray diffraction investigations makes it possible to state that, according to the database [11], the composition and the crystal lattice of the particles

revealed in alloys A_2 and A_3 coincide best with values that correspond to the bcc Al_4Cu_9 , which by itself does not exclude the possibility of the presence in the alloys of AlNi, AlFe, Al_2Cu_3 , and Al_7Cu_4Ni phases, which yield a smaller number of basis reflections that almost coincide with some reflections of the full set for Al_4Cu_9 . This assumption does not contradict the conclusions made in [5, 7], which indicate the presence of no less than six types of structural constituents in these alloys.

The results of the energy-dispersive analysis of the amounts and character of the distribution of alloying elements over the structural constituents indicate that the change in the aluminum content corresponds to a chemical analysis of the alloys and that the amount of aluminum increases in both the matrix phase and the particles. In this case, the content of copper in the matrix phase (depending on the conditions of XRD study) falls in the range of 4–12 wt %, whereas in the particles of the platelet shape, it reaches 24–61 wt %. With an increase in the aluminum concentration in the alloys, the amount of copper in the particles decreases; in alloy A_3 , it does not exceed 35 wt % (Fig. 3, Table 2), whereas in alloy A_1 , it reaches 61 wt %. According to the results of local analysis, the relative content of Al is higher in the matrix phase than in copper-containing particles (Table 2).

Since the distribution of the alloying elements (as is shown by mapping) is similar for all alloys, we only analyze the data for alloy A_3 (Figs. 3 and 4).

The above results indicate the nonuniform distribution of copper between the particles and the matrix phase and its higher content in platelet precipitates. This follows from the lighter background in the sites where particles are located compared with the matrix in the map of the copper distribution (Fig. 4). The most uniform distribution in the matrix phase is characteristic of Co, while Fe, Ni, and Cr are characterized by a nonuniform distribution. In the regions

Table 2. Quantitative content of elements at the points of registration of the spectra (Fig. 3) in the alloy A_3

Element	Point 1		Point 2		Point 3		Point 4		Point 5	
	wt %	at %	wt %	at %	wt %	at %	wt %	at %	wt %	at %
Al	1.44	3.05	1.73	3.60	1.62	3.43	1.06	2.22	0.85	1.84
Cr	17.32	19.05	18.86	20.32	15.85	17.37	25.31	27.40	13.99	15.67
Fe	17.68	18.11	21.55	21.62	18.06	18.43	22.13	22.31	15.55	16.22
Co	17.61	17.09	24.55	23.55	21.24	20.54	18.45	17.62	17.16	16.96
Ni	17.81	17.35	23.88	22.79	19.52	18.94	15.73	15.08	16.67	16.53
Cu	28.15	25.34	9.43	8.32	23.72	21.28	17.33	15.36	35.77	32.78

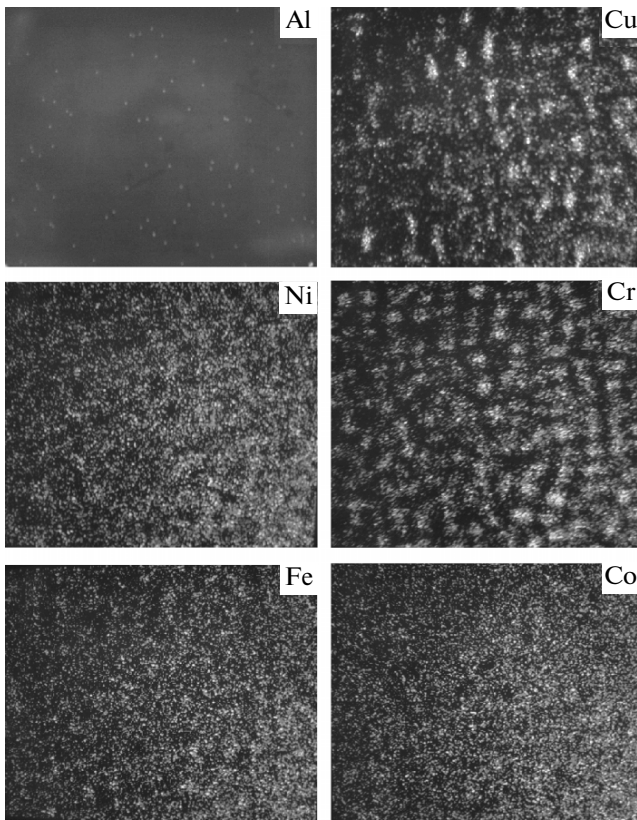


Fig. 4. Maps of the distribution of chemical elements over the volume of the region of the structure of the alloy A_3 shown in Fig. 3.

around particles, the content of these elements increases in the order of their enumeration with a clearly pronounced spottiness in the distribution of Cr (Fig. 4; Fe, Ni, Cr). This may be related to the rejection of Cr from the regions that border the platelet particles, due to the escape of Cu and Al from the matrix toward the particles.

The above results indicate that, with a large probability, the specific features of the formation of copper-containing particles in the course of crystallization and subsequent decomposition of the solid solution of the matrix phase are determined by the limiting concentrations of Cu and Al in both the liquid melt and in the solid solution, as well as by the character of their change depending on temperature and on their interaction with each other and with other elements.

The increase in the Al concentration in the alloys is accompanied not only by an increase in the uniformity of the precipitation of particles in the volume of the sample but also, according to the results of the X-ray diffraction analysis, by the transition from two types of particles with an fcc lattice in the alloy A_1 to particles with the bcc lattice with some fraction of fcc particles in the alloy A_3 . The electron-microscopic investiga-

tions do not exclude the consecutive formation of Al_2Cu_3 , Al_7Cu_4Ni , $AlNi$, and $AlFe$ particles, with the greatest probability of formation of Al_4Cu_9 precipitates, which does not contradict the results of [5, 7]. These precipitates can differ in both dispersity and morphology.

CONCLUSIONS

(1) It has been established that, in cast high-entropy $Al_xFeNiCoCuCr$ alloys ($x = 1, 1.5, 1.8$), the uniformity of the distribution and the amount of disperse precipitates of platelet and globular shape that are formed upon the decomposition of the solid solution in the process of cooling increase with increasing concentration of aluminum.

(2) With increasing aluminum concentration in the high-entropy alloys, the two types of copper-containing fcc particles that are formed upon cooling of the ingot of an equiatomic alloy pass predominantly into one type, i.e., bcc Al_4Cu_9 particles, in the alloy with $x = 1.8$.

(3) A nonuniform distribution of the elements was revealed in the high-entropy alloys, in particular, of Cu (which both forms separate particles and enters into the composition of the bcc matrix) and Cr (which forms clearly pronounced pileups (clusters) in the matrix interspaces between the platelets of the precipitates). At the same time, Al is distributed more uniformly between the particles and matrix with some priority to the latter, while Co, Ni, and Fe are mainly distributed in the volume of the matrix.

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