

PACS numbers: 61.80.Ba, 62.20.Qp, 64.60.My, 81.40.Gh, 81.65.-b

## Structure of High-Entropy CoCrFeNi Alloy Obtained by Laser Alloying

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The structural-phase state of the CoCrFeNi high-entropy alloy obtained by laser alloying of technically pure iron surface layers with a mixture of powders of pure elements Co, Ni, Cr in an equiatomic ratio was investigated by XRD, EDX and metallographic analyses. As shown, the formation of multi-component substitutional solid solution based on f.c.c. lattice, which is typical for high entropy alloys in the surface layers during laser alloying took place. The influence of the atmosphere, in which alloying is carried out, on the processes of structure formation and phase composition of alloyed surfaces are analyzed. As determined, during laser alloying in the air exothermic oxidation processes occurs, which, as a result, lead to the formation of oxygen- and chromium-enriched areas on the peripheral areas of laser spots. Laser alloying in argon atmosphere provides a uniform distribution of all elements on the surface of the laser alloying zone.

**Key words:** high-entropy alloy, laser alloying zone, chemical inhomogeneity, substitutional solid solution, high cooling rates, phase composition.

Методами XRD, EDX та металографічної аналізи досліджено структурно-фазовий стан високоентропійного сплаву CoCrFeNi, одержаного за допомогою лазерного легування поверхневих шарів технічно чистого заліза сумішню порошків чистих елементів Co, Ni, Cr в еквіатомному співвідношенні. Показано, що при лазерному легуванні у поверхневих шарах відбувалося формування багатокомпонентного твердого розчину заміщення на основі ГЦК-ґратниці, що характерно для високоентропійних сплавів. Проаналізовано вплив атмосфери, в якій здійснювалося легування, на

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Citation: v. V. Girzhon, V. V. Yemelianchenko, and O. V. Smolyakov, Structure of High-Entropy CoCrFeNi Alloy Obtained by Laser Alloying, *Metallofiz. Noveishie Tekhnol.*, 44, No. 6: 725–733 (2022). DOI: [10.15407/mfint.44.06.0725](https://doi.org/10.15407/mfint.44.06.0725)

процеси структуроутворення та фазовий склад легованих шарів. Встановлено, що при лазерному легуванні на повітрі відбуваються екзотермічні процеси окиснення, які, як наслідок, приводять до утворення збагачених Оксигеном і Хромом ділянок на периферійних околах лазерних плям. Лазерне легування в атмосфері аргону забезпечило рівномірний розподіл усіх елементів по поверхні зони лазерного легування.

**Ключові слова:** високоентропійний стоп, зона лазерного легування, хемічна неоднорідність, твердий розчин заміщення, високі швидкості охолодження, фазовий склад.

*(Received December 20, 2021; in final version, April 28, 2022)*

## 1. INTRODUCTION

Typically, high entropy alloys (HEAs) are alloys containing from 5 to 13 elements, the number of each varies within 5...35 atomic percent (equiatomic or close to equiatomic concentration of elements). A characteristic feature of HEAs is the presence in their phase composition of one or more multicomponent substitutional solid solutions based on b.c.c., f.c.c. or h.c.p. lattice. The formation of such solid solutions is explained by the high values of mixing entropy in comparison with traditional alloys [1].

Structural features of HEAs provide their high mechanical properties (hardness, wear resistance, *etc.*) in a wide range of temperatures. The increase of these properties caused by significant distortion of the crystal lattice due to the difference in the atomic radii of the substitutional elements [2].

HEAs based on f.c.c. solid solution are characterized by low strength and high ductility, and HEAs with b.c.c. structure, on the contrary, by high strength and low ductility. Therefore, to achieve a set of required physical and mechanical properties of a particular product, it is necessary to be able to obtain alloys with a certain predetermined crystal structure [3].

The vast majority of known HEAs were obtained by vacuum-arc melting, or melting in an argon atmosphere. However, in many cases it is efficient to obtain high performance of ready parts not in the whole volume, but only in certain surface areas that are exposed to the most intense mechanical stress, *i.e.*, the creation of local coatings with high mechanical properties. Among the known methods of obtaining such coatings, laser alloying is one of the most promising due to the high manufacturability of the process [4]. Significant cooling rates of the melt ( $10^3...10^6$  K/s), typical for this method, prevent the progress of diffusion processes during structural formation, which can lead to redistribution of chemical elements and the formation of other, undesir-

able, intermetallic phases. In addition, the advantages of the method include high adhesion between the coating and the matrix material [5].

The small number of scientific publications devoted to the production of HEAs coatings by laser alloying, proves that this problem requires further study. Therefore, the purpose of this study is to obtain and analyze the structural-phase state of a high-entropy alloy of the Co–Cr–Fe–Ni system obtained on the surface of samples from ARMCO iron by laser alloying.

## 2. EXPERIMENTAL/THEORETICAL DETAILS

Samples of technically pure iron (ARMCO-iron) were selected as the alloying object (matrix). Alloying was performed on a pulsed YAG laser ( $\lambda = 1.06 \mu\text{m}$ ). The alloying components were an equiatomic mixture of pure elements Co, Ni and Cr powders with a fraction size less than  $50 \mu\text{m}$ . The alloying was performed in protective argon atmosphere and in air atmosphere. The phase composition of the surface layers of the samples was controlled by XRD ( $\text{CuK}\alpha$ -radiation), EDX and metallographic analyses.

## 3. RESULTS AND DISCUSSION

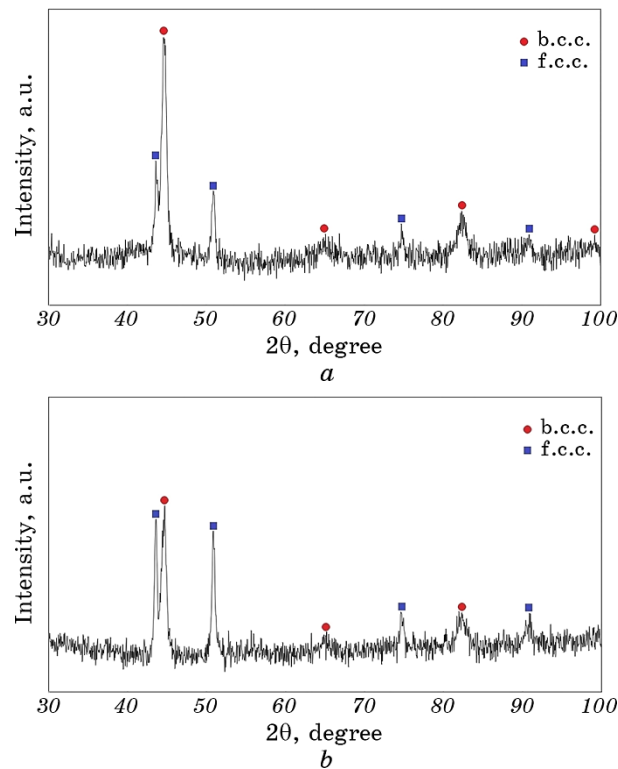
At the first step of the research, the alloying of the samples was carried out in atmospheres of air and argon with a power density  $1 \text{ GW}/\text{m}^2$  and a pulse repetition frequency  $2 \text{ Hz}$ . The thickness of the backcoat was  $120 \mu\text{m}$ .

According to XRD data, two phases were detected after alloying in the air atmosphere in the laser alloying zone (LAZ): b.c.c. and f.c.c. solid solutions (Fig. 1, *a*). Precisely determined lattice parameters of the obtained phases are presented in Table 1. It should be noted that the lattice parameter of the f.c.c. phase actually coincided with the lattice parameter of the HE-alloy of the same system, given in [7]. The lattice parameter of the b.c.c. phase was slightly larger than the lattice parameter  $\alpha$ -Fe. Therefore, we can assume that the b.c.c. phase is a substitutional solid solution of chromium in iron, because according to [8] Fe and Cr form continuous series of solid solutions, and the size of chromium atoms is larger than the size of iron atoms. Due to the low solubility of oxygen and nitrogen in the  $\alpha$ -Fe lattice, their effect on the lattice parameter change can be neglected. The sizes of Co and Ni atoms are smaller than those ones of iron atoms.

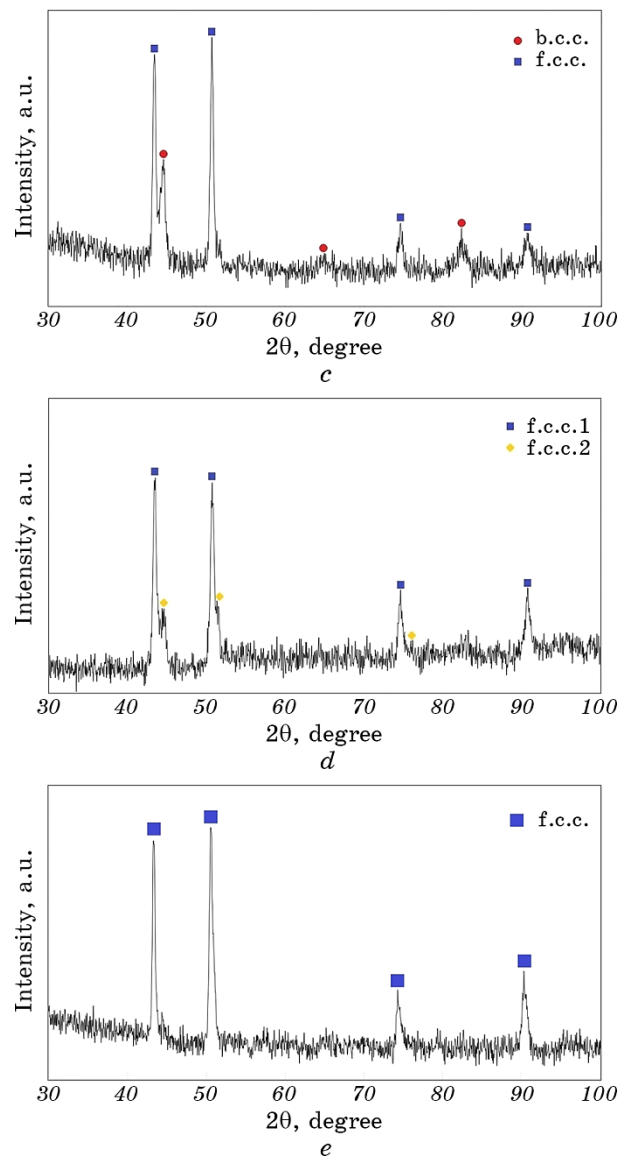
EDX analysis of the alloyed surface of the sample (Fig. 2) showed that the distribution of alloy components on the LAZ surface is homogeneous except for the peripheral regions of the laser spots. Elevated chromium and oxygen content was observed in these areas. This fea-

ture of the distribution of chemical elements can be explained in the following way. As known [9], that from all of the elements of the system, chromium has the greatest tendency to interact with oxygen and can form refractory oxides. The crystallization of the melt pool in the surface layers began with the areas that had the lowest temperature, *i.e.*, in the peripheral areas of the laser spots. In the first stages of crystallization, the most refractory phases were formed. Taking in consideration the fact that laser alloying was performed in air atmosphere, we can assume that this was the main reason for the formation of oxygen and chromium-enriched areas. The absence of reflections from the lattices of oxides on the diffractograms indicated a small volume fraction of them.

In order to eliminate the influence of the air atmosphere on the peculiarities of the distribution of elements on the LAZ surface, laser alloying in an argon atmosphere was performed. It turned out that this treatment provided a homogeneous distribution of all the elements on the LAZ surface (Fig. 3). This indicated the legitimacy of the assump-



**Fig. 1.** XRD-patterns from the surface layers of samples of armco-iron after laser alloying with an equiatomic mixture of powders Co, Cr, Ni.



Continuation of Fig. 1.

tion about the reasons for the heterogeneity of the distribution of elements during alloying in air atmosphere.

It should be noted that alloying in an argon atmosphere led to a decrease in the intensities of diffraction maxima from the b.c.c. phase lattice (Fig. 1, b). This redistribution is explained by the fact that in the absence of oxygen, the temperature on the surface of the sample

**TABLE 1.** Lattice parameters of phases in LAZ after alloying under different conditions.

Thickness of backcoat, $\mu\text{m}$	Atmosphere of treatment	Phase composition	Lattice parameters, nm
120	Air	b.c.c.	$0.28695 \pm 0.00011$
		f.c.c.	$0.35724 \pm 0.00016$
120	Argon	b.c.c.	$0.28699 \pm 0.00011$
		f.c.c.	$0.35732 \pm 0.00016$
150	Air	b.c.c.	$0.28713 \pm 0.00011$
		f.c.c.	$0.36011 \pm 0.00016$
150	Argon	f.c.c. 1	$0.35992 \pm 0.00016$
		f.c.c. 2	$0.35521 \pm 0.00016$

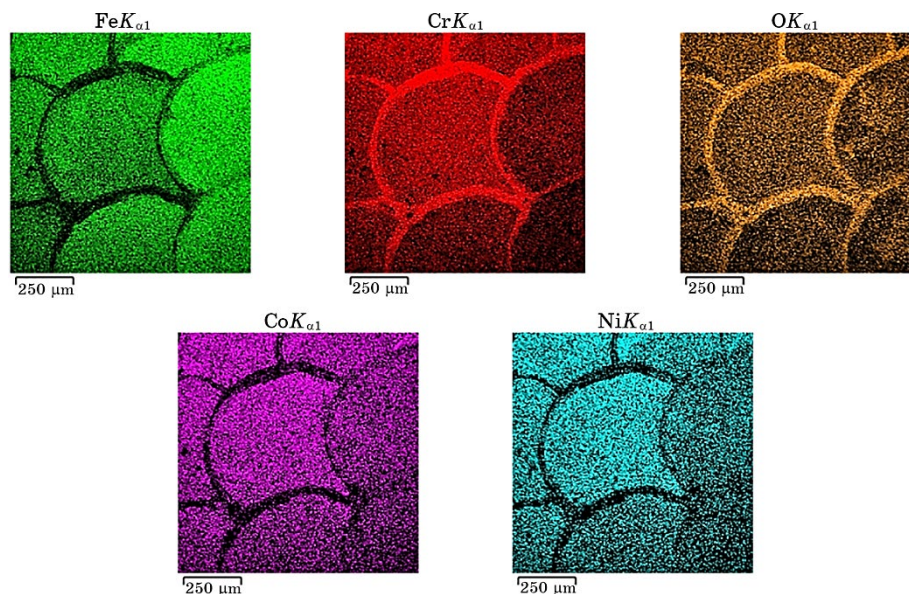
during alloying was lower than during alloying in the air [10]. This can be caused by the absence of exothermic oxidation processes of both the organic components of the binder and the metals. As a result, the penetration depth decreased and, as a consequence, the amount of iron in the LAZ reduced. This caused a decrease in the volume fraction of b.c.c. phases. Indeed, according to EDX studies, the ratio of the amount of iron to the total amount of all other components in the LAZ after treatment in an argon atmosphere reduced from 2.45 to 1.76.

The decrease in the temperature of LAZ during alloying in argon can also explain the presence of areas that contained an increased number of individual components (Fig. 3), as the residence time of LAZ in the liquid state diminished.

Precise calculations of lattice parameters (Table 1) after alloying in argon atmosphere revealed their slight increase. This could be explained by the fact that the part of chromium atoms, which bound to oxides during alloying in air atmosphere, in this case participated in the process of LAZ structure.

The obtained data on the LAZ phase composition demonstrated an excess of iron in it (b.c.c. phase formation). This indicated that the chemical composition of the LAZ surface layers did not fully correspond to the region of homogeneity of the solid solution typical for Co–Cr–Fe–Ni system HEAs [11]. In order to reduce the amount of iron in LAZ at the next step of the study alloying was performed with a backcoat thickness 150  $\mu\text{m}$ .

After alloying in air atmosphere (Fig. 1, c) in the LAZ surface layers, f.c.c., and b.c.c. phases were again detected, and the volume fraction of b.c.c. phases was smaller than after alloying with a backcoat thickness 120  $\mu\text{m}$ , which was the expected result. The lattice paramete-

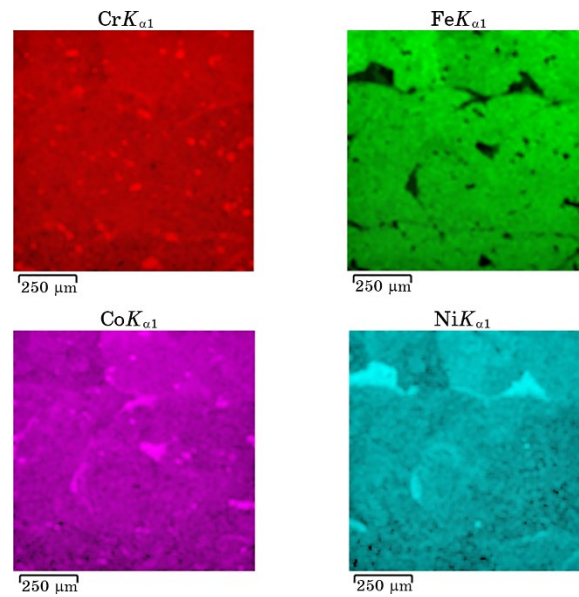


**Fig. 2.** Distribution of chemical components on the surface of LAZ after laser alloying in the air atmosphere.

ters of both solid solutions (Table 1) increased markedly. The growth in the b.c.c. phase parameter is quite easily explained by the augmentation in the relative amount of chromium in the LAZ. The parameter of the f.c.c. phase differed significantly from the previous one. This allowed us to assume that the formed f.c.c. phase is not identical in chemical composition to the same phase formed in LAZ during alloying with a smaller thickness of the backcoat.

Alloying with a backcoat thickness 150  $\mu\text{m}$  in an argon atmosphere (Fig. 1, *d*) led to the formation in the alloyed layers of two f.c.c. solid solutions with different lattice parameters (Table 1). The presence on the diffractograms of reflections from the lattice of the two f.c.c. phases only indicated the absence of condition for the formation of the b.c.c. phase. This can be explained by decrease in the amount of iron in LAZ, caused by lower temperatures of structure formation in the absence of oxygen.

The formation of two f.c.c. solid solutions could be due to the rather inhomogeneous distribution of chemical elements in the LAZ, caused by high cooling rates of the melt and the Marangoni–Gibbs effect [12, 13]. Therefore, in order to align the chemical composition, the laser remelting of alloyed surface with a lower power density (0.5  $\text{GW}/\text{m}^2$ ) in argon atmosphere was carried out. After such treatment, only one f.c.c. phase was observed in the LAZ (Fig.1, *e*). The lattice parameter of the obtained solid solution ( $0.35994 \pm 0.00016$ ) nm practically coin-



**Fig. 3.** Distribution of chemical components on the surface of LAZ after laser alloying in the argon atmosphere.

cided with the lattice parameter of the multicomponent substitutional solid solution, the formation of which is typical for HEAs of this system [14]. Thus, the described method makes possible to obtain a coating type HEAs on the surface of the iron.

#### 4. CONCLUSIONS

1. Laser alloying of the ARMCO-iron surface layers with a mixture of powders Co, Ni, Cr, taken in the equiatomic ratio allows to obtain a highly adhesive coating, which contains phases typical for high-entropy alloys.
2. After laser alloying in air atmosphere contrast to alloying in a neutral environment the alloying zone is characterized by an increased content of matrix iron, which is caused by higher temperatures due to exothermic oxidation processes and the consequent increase in melt pool depth.

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