

## Microstructure and Properties of AlCrFeCoNiCu<sub>x</sub> High-Entropy Alloys

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**Abstract.** The peculiarities of the structure formation of alloys of the system AlCrFeCoNiCu<sub>x</sub> (where  $x = 0, 0.5, 1, 2,$  and  $3$  moles) were studied. Microstructure of alloys and its phase composition, as the amount of copper increases, undergo significant changes. In all of the investigated concentration interval of change in the content of copper there is a different phase morphology. Confirmed that with increasing of Cu concentration the nature of crystallization of alloys and their phase composition change. Durometric studies of alloys of this system were carried out. Established that an alloy AlCrFeCoNiCu<sub>0.5</sub> has the highest microhardness 6.1 GPa. Heat resistance tests showed that AlCrFeCoNi and AlCrFeCoNiCu have the highest heat resistance. The connection between the scale composition after the test and the mechanism of oxidation of this alloys revealed. The results of X-ray fluorescence analysis indicate a high content of aluminum in scale. Consequently, the high heat resistance of alloys can be explained by the formation of the Al<sub>2</sub>O<sub>3</sub> protective film on the surface.

**Keywords:** high-entropy alloys, microstructure, microhardness, heat resistance.

## 1 Introduction

Contemporary development of technology puts forward new requirements for the details of machines and mechanisms operating in extreme conditions. One of the effective methods for improving the physical-mechanical and operational properties of parts is the replacement of traditional structural materials (steels and alloys) with new promising materials. These materials include high-entropy alloys (HEAs). High-entropy alloys are alloys containing in their composition five or more metal elements (usually from five to thirteen) in equimolar or almost equimolar proportions (i. e., the concentration of each element is in the range of 5 to 35 atomic percentages). HEAs are characterized by high entropy of mixing in the initial and liquid (melted) state ( $S_{\text{mix}} > 1.61R$ , where  $R = 8.314 \text{ J/(mol}\cdot\text{K)}$  – gas constant). The principal difference between HEAs from traditional alloys containing a solvent and a dissolved substance is the formation of a disordered solid solution in which the atoms of the constituent elements have equal probability to occupy any node of the crystalline lattice. Significant distortion of the crystal lattice arising from the presence of heterogeneous

atoms of elements with different electronic structures, sizes and thermodynamic properties affects both the structure and the properties of the resulting alloy. The growth of the number of components of the alloy increases the level of its solid solution hardening. HEAs can be applied in conditions of shock and dynamic loads, friction, elevated temperatures, since disordered solid solutions are more plastic than intermetallics that are formed in high-alloy steels and alloys. From high-entropy alloys can be made both volumetric materials and coatings for application in various spheres.

Over the past few years (mainly in foreign publications), a significant number of articles describing the properties of HEAs [1–4]. In these works the thermodynamics of high-entropy alloys is described, their microstructures are modeled, and methods of obtaining are offered. During the study of HEAs, it was found that they have high mechanical properties, such as high hardness, wear resistance, high temperature strength, corrosion resistance, ductility at low temperatures, and superplastic properties [5]. However, some properties of HEAs are not studied enough.

For HEAs of the AlCrFeCoNiCu system already been investigated the influence of Fe on the microstructure and mechanical properties [6], features of structure formation [7]. In [8] the properties of AlCrFeCoNiCu<sub>0.5</sub> alloy coatings deposited on the silicon plate by radiofrequency sputtering were considered. However, in general, the properties of AlCrFeCoNiCu system alloys remain insufficiently investigated.

The purpose of this work was to study the structure of high-entropy alloys of the AlCrFeCoNiCu<sub>x</sub> system and the relationship between their chemical composition and physical and mechanical properties.

## 2 Research Methodology

The investigated samples of alloys of the AlCrFeCoNiCu<sub>x</sub> system were made by the method of argon-arc melting in the furnace MIFI-9-3. As charge materials used: Cr – hydrogen refined in the form of bits; Ni – cathode in the form of plates 10 mm thick; Co – pressed granules; Cu – vacuum-fused in the form of granules; Fe – carbonyl in the form of granules. Cr, Co, Ni, Cu had a purity of not less than 99.95 % wt, Fe – not less than 99.8 % wt. Melting occurred with a tungsten non-consumable electrode, on a copper water-cooled subunit. After completion of the smelting, the chemical composition was controlled by the loss of mass in the smelt, which in most cases was small and did not exceed 0.3 % wt.

The study of microstructure was carried out on a metallographic microscope MIM-7 at different magnifications on etched materialographic specimen. Dyrometric studies were performed on the microhardness tester PMT-3 in at least 10–15 fields of view at a load of 0.49–

0.98 N. As an indenter, a diamond pyramid with a square base and a two-cornered apex with an apex of 136° was used. Measurement accuracy of microhardness ±250 MPa.

The heat resistance test was carried out using a weight method for increasing the mass of samples after exposure to the furnace for 100 hours at a temperature of 1000 °C. Samples for determining the heat resistance of investigated alloys of the same size were carved from cast billets by the method of spark cutting. The surface of the samples was sanded with fine sandpaper and degreased before the test. Before the test, the samples were dried and weighed on analytical weights to within ± 0.1 mg. Also, their surface area was measured. After that, samples in separate crucibles of aluminum oxide were placed in an electric furnace. The furnace was heated to a temperature of 1000 °C, the exposure was 100 hours. Samples were weighed after every 3-7 hours of the test. The chemical composition of the scale was determined by the desktop energy-dispersive X-ray fluorescence spectrometer ElvaX Light SDD.

## 3 Results and discussions

Fig. 1 shows the microstructures of the AlCrFeCoNiCu<sub>x</sub> alloys obtained with an optical microscope. Microstructure of alloys and its phase composition, as the amount of copper increases, undergo significant changes. In all of the investigated concentration interval of change in the content of copper there is a different phase morphology.

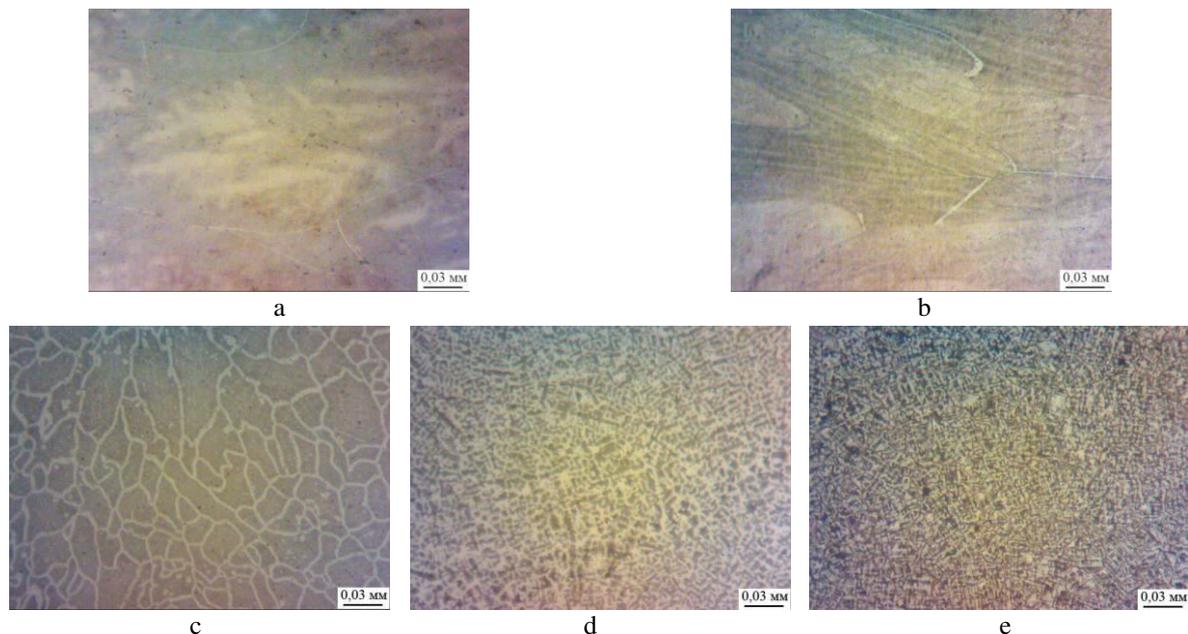


Figure 1 – Microstructures of AlCrFeCoNiCu<sub>x</sub> cast high-entropy alloys in a light microscope:  $x = 0$  (a);  $x = 0.5$  (b);  $x = 1$  (c);  $x = 2$  (d);  $x = 3$  (e)

The microstructural analysis of the AlCrFeCoNi alloy showed (Fig. 1 a) that the microstructure is homogeneous with a structure consisting of equilibrium grains. Their average grain size is 320  $\mu\text{m}$ .

The microstructures of alloys in which  $x = 0.5$  and 1 mol Cu are added have a similar structure, except that they have the grain boundaries of the light phase layer (Fig. 1 b–c). In [7] argues that the dark phase has a BCC structure, and the light phase has a FCC structure. In addition, with an increase of Cu content from 0 to 1 mole, the grains are refined: its size is 150  $\mu\text{m}$  for the AlCrFeCoNiCu<sub>0.5</sub> alloy, and 30–40  $\mu\text{m}$  for the AlCrFeCoNiCu alloy.

When adding 2 moles of copper (Fig. 1 d), there is a dendritic nature of crystallization. As shown in [7], dendrite is associated with a solid solution based on the phase with the bcc structure, and the interdendrite area is a solid solution based on the phase with the fcc structure.

When copper content  $x = 3$  mole, the nature of crystallization does not change.

Consequently, the content of Cu greatly affects the structure and phase composition of alloys of the AlCrFeCoNiCu<sub>x</sub> system. With the increase in the concentration of copper, the nature of crystallization changes, in addition, according to earlier studies, the phase composition also changes.

Dyrometric analysis showed that the highest microhardness (6.1 GPa) has an AlCrFeCoNiCu<sub>0.5</sub> alloy (Fig. 2). In other alloys, the microhardness is proportional to the volume fraction of a solid solution based on the phase with the bcc structure, which in turn is inversely proportional to the amount of copper in the alloy. The high microhardness of the AlCrFeCoNiCu<sub>0.5</sub> alloy can be explained by the presence of fine-grained structure, since copper in an amount equal to half of the aviation volume is a good modifier of the second kind, which, according to the law of Hall-Petch, leads to strengthening. The mechanism of reducing the size of the grain is as follows: copper or its compounds adsorbed on the surface of growing crystals and inhibit their growth. This leads to an increase in the amount of supercooled melt before the crystallization front and creates favorable conditions for the emergence of new centers of nucleation of crystals, which leads to grain refinement.

As you know, some HEAs have a high corrosion resistance and heat resistance. The author of [9] explains the behaviour of the aggressive medium at elevated temperature by the structure of HEAs, which consists of a homogeneous solid solution. The authors of [10] believe that the increased values of heat resistance are characteristic of HEAs based on refractory metals. In this regard, the task of studying the heat resistance of alloys of the AlCrFeCoNiCu system and the influence of Cu on the parameters of heat resistance is relevant.

The heat resistance tests conducted in an air atmosphere at a temperature of 1 000 °C for 100 hours showed (Fig. 3) that the investigated alloys are characterized by high heat resistance ( $\Delta g$  – mass loss per unit of surface

area of tested samples,  $\text{mg}/\text{cm}^2$ ). Fig. 3 shows that AlCrFeCoNi and AlCrFeCoNiCu have the highest heat resistance, the heat resistance of AlCrFeCoNiCu<sub>2</sub> alloy is slightly lower, and the highest mass loss per unit of surface area (and therefore the lowest heat resistance) have AlCrFeCoNiCu<sub>3</sub> alloy.

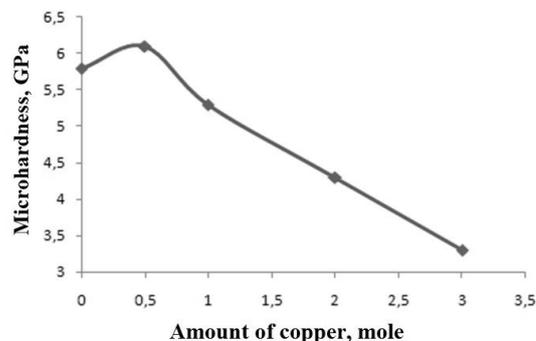


Figure 2 - Concentration dependence of microhardness for alloys of the AlCrFeCoNiCu<sub>x</sub> system

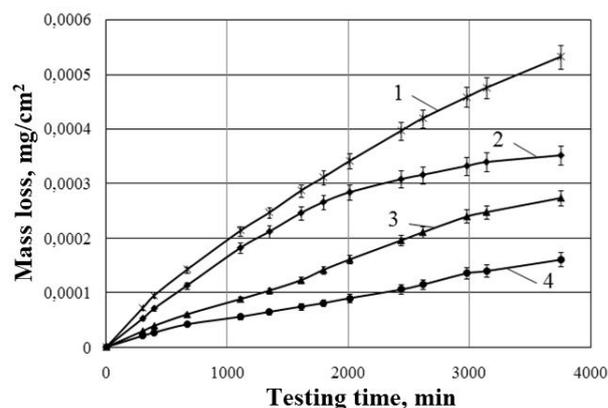


Figure 3 – Curves of AlCrFeCoNiCu<sub>x</sub> system alloys during the heat resistance tests (air, 1 000 °C, 100 hours):

1 – AlCrFeCoNiCu<sub>3</sub>; 2 – AlCrFeCoNiCu<sub>2</sub>; 3 – AlCrFeCoNi; 4 – AlCrFeCoNiCu

In [11] it was suggested that the mechanism of oxidation of this HEAs can be described on the basis of the Higgins-Pettit's theory of Ni-Cr-Al alloys oxidation. This is an empirical theory that divides Ni-Cr-Al alloys into 3 groups, based on the scheme of their oxidation [12]. Group I corresponds to dilute alloys in which Cr and Al concentrations are too low to establish continuous Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> scales. Instead, the external scales consist of NiO plus Ni<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub> and Ni<sub>2</sub>Al<sub>2</sub>O<sub>4</sub> spinel phases coupled with internal oxidation of Al. Group II corresponds to alloys with large enough Cr concentrations, but relatively low Al concentrations, that results in selective oxidation of Cr, which forms external Cr<sub>2</sub>O<sub>3</sub> scale. The formation of internal Al<sub>2</sub>O<sub>3</sub> subscale proceeds as a result of internal oxidation. Group III corresponds to alloys containing large enough Al concentration to promote the selective oxidation of Al, that results in formation of external Al<sub>2</sub>O<sub>3</sub> scale.

The results of X-ray fluorescence analysis (Table 1) showed a high Al content in scale as compared to an unoxidized alloy, which confirms the above-mentioned assumptions. This fact confirms Al diffusion on the surface of the alloy during oxidation and, accordingly, the formation of an  $Al_2O_3$  oxide film. Thus, the AlCrFeCoNiCu<sub>x</sub> system HEAs are characterized by high heat resistance due to the relatively high content of Al in oxide. AlCrFeCoNi and AlCrFeCoNiCu alloys have the

highest thermal resistance, and when the copper content is high, the hardness of the alloys is deteriorating. Previously it was shown [7] that copper at concentrations more than half the equio-atom leads to the digestion, the formation of several FCC phases instead of one initial BCC of a solid solution. It is obvious that such an effect of Cu on the microstructure and phase composition worsens the characteristics of heat resistance at its high content due to the fact that the Cu enriched interdendritic area is fusible.

Table 1 – Results of the spectral analysis of scale after the heat resistance test

Atomic number	Element	Series	Intensity	Concentration, % wt
Alloy AlCrFeCoNi				
13	Al	K	56124	16.4093 ± 0.1305
24	Cr	K	323339	29.2553 ± 0.1020
26	Fe	K	188479	21.1143 ± 0.0970
27	Co	K	228360	20.3330 ± 0.1021
28	Ni	K	142385	12.8881 ± 0.0860
29	Cu	K	0	< 0.0343
Alloy AlCrFeCoNiCu				
13	Al	K	210233	31.8171 ± 0.1130
24	Cr	K	175297	16.5350 ± 0.0819
26	Fe	K	163873	14.0406 ± 0.0720
27	Co	K	233312	15.8340 ± 0.0797
28	Ni	K	137857	9.9116 ± 0.0696
29	Cu	K	176183	11.8617 ± 0.0640
Alloy AlCrFeCoNiCu <sub>2</sub>				
13	Al	K	232208	33.0242 ± 0.1124
24	Cr	K	121213	13.1214 ± 0.0788
26	Fe	K	140157	12.2647 ± 0.0698
27	Co	K	184363	12.7072 ± 0.0757
28	Ni	K	116441	8.9282 ± 0.0678
29	Cu	K	282603	19.9544 ± 0.0800
Alloy AlCrFeCoNiCu <sub>3</sub>				
13	Al	K	257037	32.7679 ± 0.1070
24	Cr	K	96288	11.2138 ± 0.0754
26	Fe	K	114405	9.8994 ± 0.0637
27	Co	K	154714	10.5938 ± 0.0710
28	Ni	K	121810	9.4739 ± 0.0682
29	Cu	K	367425	26.0512 ± 0.0883

## 4 Conclusions

The influence of copper concentration on the phase composition and structure of alloys of the AlCrFeCoNiCu<sub>x</sub> system has been investigated. Confirmed that with increasing of Cu concentration the nature of crystallization of alloys and their phase composition change.

Durometric studies have shown that the highest microhardness (6.1 GPa) of alloys of the AlCrFeCoNiCu<sub>x</sub> system has an AlCrFeCoNiCu<sub>0.5</sub> alloy, which is due to the presence of fine-grained structure. With an increase in the concentration of Cu, the microhardness of alloys is reduced.

Experimentally determined the heat resistance of the AlCrFeCoNiCu<sub>x</sub> system HEAs, revealed a connection between their composition, structure and heat resistance. AlCrFeCoNi and AlCrFeCoNiCu alloys have the highest heat resistance. The high content of Cu in alloys contributes to the formation of several FCC phases instead of one initial solid solution with BCC structure. In addition, the Cu enriched interdendritic area is fusible, which worsens the heat resistance of investigated alloys.

The mechanism of oxidation of alloys of the investigated system at elevated temperature was found. The results of X-ray fluorescence analysis indicate a high content of aluminum in scale. Consequently, the high heat resistance of alloys can be explained by the formation of a  $Al_2O_3$  protective film on the surface.

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## Дослідження структури та властивостей високоентропійних сплавів системи AlCrFeCoNiCu<sub>x</sub>

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**Анотація.** Досліджені особливості структуроутворення сплавів системи AlCrFeCoNiCu<sub>x</sub> (де  $x = 0; 0,5; 1; 2$  і  $3$  моль). Як і фазовий склад, мікроструктури сплавів по мірі збільшення кількості міді зазнають істотних змін. В усьому досліджуваному концентраційному інтервалі зміни вмісту міді спостерігається різна морфологія фаз. Підтверджено, що при збільшенні концентрації міді змінюється характер кристалізації сплавів даної системи. Проведені дюрOMETричні дослідження сплавів даної системи. Встановлено, що найвищу мікротвердість 6,1 ГПа має сплав AlCrFeCoNiCu<sub>0,5</sub>. Випробування на жаростійкість показали, що найвищу жаростійкість мають сплави AlCrFeCoNi та AlCrFeCoNiCu. Виявлено зв'язок між складом окалини після випробувань і механізмом окислення даних ВЕСів. Результати рентгенофлуорисцентного аналізу свідчать про високий вміст алюмінію в окалині. Отже високу жаростійкість сплавів можна пояснити утворенням на поверхні захисної плівки Al<sub>2</sub>O<sub>3</sub>.

**Ключові слова:** високоентропійний сплав, мікроструктура, мікротвердість, жаростійкість.