

## Synthesis of Cast High Entropy Alloys with a Low Specific Gravity by Centrifugal Metallothermic SHS-Methods

V.N. Sanin\*, D.M. Ikornikov, D.E. Andreev, N.V. Sachkova, V.I. Yuxhvid

*Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,  
8, Academician Osipyan St., Chernogolovka, Moscow Region, 142432, Russia*

\* Corresponding author: Tel. +7 496 524 6510; fax: +7 496 524 6222. E-mail: svn@ism.ac.ru

### Abstract

For the last few years, the so-called high-entropy alloys (HEAs) have attracted considerable attention of researchers in the field of materials science of metallic materials. Their distinguishing feature is the presence of five or more elements with an equitonus concentration. However, the entire range of HEA-based materials and their possible properties have not been fully studied. Most studies of HEAs focus on determining the microstructure-properties relationship. Little attention has been paid to the study and development of new methods for obtaining HEAs. Yet, the production of such multicomponent alloys is a complex scientific and technological problem.

The paper investigates the possibility of producing high-entropy cast alloys  $\text{CoCrFeNiMnAl}_x$  and  $\text{CuAlZrTi(L-Cr)}_x$  by the SHS-metallurgy methods, and presents the findings of the first positive experiment. The microstructure of the produced alloys is investigated. The analysis of the obtained data allows drawing a conclusion about the prospects of the materials under investigation and the method of their production for the formation of volumetric nanostructured materials.

### Keywords

Cast high entropy alloys (HEAs); cast polymetallic alloys; centrifugal metallothermic SHS; SHS-metallurgy; combustion synthesis.

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### Introduction

Multicomponent alloying is widely used in the development of many materials operated at extreme conditions (elevated temperatures and loads); in particular, heat-resistant iron- and nickel-based alloys [1–3]. The possibilities of traditional approaches for creating metallic materials through the selection of alloying elements to improve the desirable characteristics of an alloy based on a single component are largely exhausted and do not lead to a significant improvement in properties. In recent years, multicomponent alloys have aroused an additional interest related to the discovery of previously studied compositions of alloying elements and the base that are in equiatomous concentration, i.e. the so-called high-entropy alloys (HEAs) [4]. The presence of heterogeneous atoms of elements with different electronic structure, dimensions, and thermodynamic properties in the crystal lattice of HEAs leads to its significant distortion. This contributes to the structural

strengthening of alloys and the thermodynamic stability of the properties of such materials [5–8]. The development of research on the nature of the formation of multicomponent highly entropic systems, the development of practically meaningful compositions of alloys based on them, is relevant for modern materials science.

Today, HEAs are in the center of attention of materials scientists from around the world [5, 9, 10]. This interest is explained by several factors. Firstly, the concept of high-entropy alloys offers great opportunities for creating new alloys with structures and properties that are different from those of “traditional” alloys based on a single component. Secondly, some of the already investigated alloys demonstrated extremely attractive mechanical properties [7, 9, 11, 12] – a combination of high ductility and strength at room temperature, record values of impact strength and fracture toughness at room and cryogenic temperatures, high specific strength at elevated temperatures, etc.

The most studied alloys belonging to this group are the alloys in the Co–Cr–Fe–Ni–Mn system. The equiatomic Co–Cr–Fe–Ni–Mn alloy does have a single-phase structure of a disordered substitution solid solution on the basis of a face-centered cubic (FCC) lattice [13, 14]. The interest in this alloy is explained by the two factors. The first one is the alloy structure. As mentioned above, the alloy most often demonstrates a single-phase structure of a solid substitutional solution, in which the atoms of the constituent elements are randomly distributed over the sites of the FCC lattice [14–16]. At present, it has been reliably established that the FCC structure is thermodynamically stable at temperatures  $\geq 900$  °C [17]. At lower temperatures, the separation of particles of the second phases, such as the sigma phase, can be observed. However, in general, the single-phase structure of the alloy is quite stable, and therefore it is widely used as a “model” HEA – a single-phase multicomponent solid solution.

The second reason of the researchers’ interest in the CoCrFeNiMn alloy is its mechanical properties. In one of the first works on this alloy, it was shown that it has an extremely high plasticity at room temperature, with the elongation to failure up to 70–80 % [18]. In this case, both the ductility and the strength of the alloy increase noticeably when cooled to cryogenic temperature. Moreover, the measured fracture toughness of the alloy at cryogenic temperature is one of the highest among metallic materials –  $200 \text{ MPa}\cdot\text{m}^{-1/2}$  [19].

From the perspective of expanding the potential of possible use of HEAs, the development of new structurally strengthened HEA-based materials with a low specific gravity is of special interest. Such works are currently in their infancy.

It can be argued that the entire range of HEA-based materials and their possible properties have not been disclosed to date. Most HEAs research focuses on elucidating the relationship of microstructure-properties. Little attention is paid to the study and development of new methods for producing HEAs. However, the production of such multicomponent alloys is a complex scientific and technological task. The most important technological factor ensuring the production of polycrystalline high-entropic alloys in the solid state is a high degree of homogenization of the alloy in terms of chemical composition [6, 7, 10]. A sufficiently high cooling rate of the alloy in the liquid and solid states does not allow diffusion processes to develop, thus, leading to the formation of chemical compounds, i.e. to the decomposition of the solid solution and, consequently, to a decrease in the entropy of mixing.

The purpose of this work is to study the possibility of producing cast equiatomic CoCrFeNiMnAl<sub>x</sub> and CuAlZrTi(Li–Cr)<sub>x</sub> alloys in the process of combustion, which was called the “SHS-technology of high-temperature melts” [20] or the “SHS-metallurgy” [21, 22].

### Experimental scheme for the HEA synthesis

The use of highly exothermic SHS compounds of the thermite type makes it possible to apply temperatures sufficient to produce melts of combustion products (above 2500 °C) and, as a consequence, to obtain cast products of synthesis (in the form of ingots).

The synthesis was carried out using powdered SHS systems of a thermite type containing oxides of the target elements – NiO, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, Cu<sub>2</sub>O, Li<sub>2</sub>CrO<sub>4</sub>, and also metals – Al, Zr, Ti. The average particle size for oxides was 50–100 µm, and aluminum was less than 140 µm (PA-4 grade). The mass of the initial mixture for combustion in all experiments was constant and amounted to 150 g. The combustion was carried out in graphite forms with a diameter of 40 mm.

The experiments were carried out on a centrifugal SHS plant [23] under the influence of an overload of 10 to 300 g, which in turn is a powerful tool for controlling the combustion processes and the formation of synthesis products [23, 24]. The effect of overload in the combustion stage made it possible to suppress the spread of products during combustion, to realize intensive mixing of the melt over the combustion front and to obtain a high conversion of the initial mixture in the combustion front. At the stage of gravitational separation and cooling, the effect of overloading made it possible to realize the high yield of the metallic phase in the ingot (*close to the calculated one*), to remove the gaseous products from it and to facilitate the equalization of the chemical composition by the HEA ingot volume, which was very important for the synthesis of polycrystalline alloys.

The general scheme of the process for the synthesis of cast alloys was described in [23].

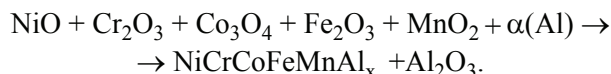
The obtained ingots were investigated by the XRF and electron microscopy (SEM) methods. The microanalyses of structural components were carried out by the EDS methods. To increase the contrast and identify the nanostructured constituents of the alloys, they were treated with a 5 % solution of nitric acid, followed by neutralization of the solution.

Two experimental compositions were investigated: 1) NiCrCoFeMnAl<sub>x</sub> and 2) CuAlZrTi(Li–Cr)<sub>x</sub>. The concentration of Al and Li(Cr) was changed in the composition of the investigated alloys.

## Results and discussion

### *Synthesis of alloys in the NiCrCoFeMnAl<sub>x</sub>-system*

In general, the chemical scheme for the synthesis of alloys based on the first NiCrCoFeMnAl<sub>x</sub>-system under study can be represented as:



In the framework of this paper, the NiCrCoFeMnAl<sub>x</sub> system was investigated, where  $x$  (mole fraction of Al) was varied from 0.2 to 2. The remaining components were represented in equal atomic fractions. The calculated composition of the investigated alloys is presented in Table 1.

From the authors' previous studies, it is known that the gravitational effect in the SHS process [21–24] allows achieving the maximum separation of the target product (ingot) from slag (Al<sub>2</sub>O<sub>3</sub>) and convective mixing of all components of the alloy, which is especially important with increasing the amount and concentration of components in the alloy. Therefore, the HEA synthesis was carried out in a centrifugal SHS plant. In the experiments, the propagation of the combustion front along the sample ( $U_C$ ), the mass loss value ( $\eta_{\text{var}}$ ) during the synthesis (variation) and the completeness of the yield of the target product (alloy) in the ingot ( $\eta_{\text{ing}}$ ) were recorded. The characteristics were calculated by the formula:

$$\eta_{\text{var}} = [(M_O - M_E)/M_O] 100 \%;$$

$$\eta_{\text{ing}} = [(M_{\text{ING.E.}} - M_{\text{ING.EXP}}) / M_{\text{ING.E.}}] 100 \%,$$

where  $M_O$ ,  $M_E$  are mass of the original mixture and combustion products after the experiment;  $M_{\text{ING.E.}}$ ,  $M_{\text{ING.EXP}}$  are the estimated mass of the ingot and the mass of the ingot obtained in the experiment.

To identify optimal conditions for the HEA synthesis, a series of experiments was carried out,

where the magnitude of the gravitational action (centrifugal acceleration) varied from 10 to 400g. A significant increase in the burning rate from 2 to 8.2 cm/s for the composition of NiCrCoFeMnAl<sub>0.2</sub> and from 2 to 6.8 cm/s for the composition of NiCrCoFeMnAl<sub>2</sub> with increasing  $g$  was established. The most intense rate increase ( $U_C$ ) was observed in the range of overload values from 10 to 150g. The increase in the burning rate is due to the forced filtration of the high-temperature melt into the initial mixture [22]. It should also be noted that, along with a significant increase in  $U_C$ , with an increase in  $g$ , a significant decrease in the spread ( $\eta_{\text{var}}$ ) was observed, and the depth of the yield of the target product ( $\eta_{\text{ing}}$ ) in the ingot approaches the estimated value.

The HEA ingots obtained after the synthesis had a mass of (100±10) g (depending on the composition and conditions of synthesis). All samples were cast. The analysis of the samples on the cross section showed that ingots obtained at  $a/g \leq 100$  in the central upper part had a small shrinkage shell and porosity, which is a characteristic feature of the cast state. In contrast, in the samples formed at  $a/g \geq 100$ , no residual porosity was observed in the cross section. The ingots obtained under these conditions had a weight close to the calculated (about 98 mass. %), and the mass loss (variation) of the composition in the combustion process did not exceed 1.5 mass. %. The metal (target) and oxide (slag) layers after the synthesis were mechanically easily divided into two layers: 1 – the target alloy; 2 – the oxide layer (Al<sub>2</sub>O<sub>3</sub>). In the optimal region, no residual porosity was observed on the cross section.

The analysis of the results leads to the conclusion that for the investigated compositions the optimal region for the synthesis of the investigated HEAs is 100–150g. It should be noted that in scaling (consolidation) of synthesized ingots this parameter can be reduced to 50g.

Next, the samples of the alloys were synthesized at 150g and subjected to comprehensive analysis. The analysis of the chemical composition of the samples taken from different sections of the ingot did not reveal any noticeable differences in the concentration of the components, the deviations fit within the error interval of analytical methods of the research. A slight deviation of the components of the synthesized alloys from the calculated values (less than 2 %) was observed with the exception of Mn, the deviation of which was 6 % (of the calculated value). Later this deficiency was solved by the excessive introduction of MnO<sub>2</sub> into the composition of the original mixture.

The analysis of the optimized compositions of the samples revealed that an increase in the Al concentration

Table 1

### The calculated composition of alloys under study

Estimated composition, weight, %	Ni	Cr	Co	Fe	Mn	Al
NiCrCoFeMnAl <sub>0.2</sub>	20.6	18.2	20.7	19.6	19.3	1.6
NiCrCoFeMnAl <sub>0.6</sub>	19.9	17.6	20.0	18.9	18.6	5.0
NiCrCoFeMnAl <sub>1.0</sub>	19.0	17.3	19.1	18.1	17.8	8.7
NiCrCoFeMnAl <sub>1.2</sub>	18.7	16.5	18.8	17.8	17.5	10.7
NiCrCoFeMnAl <sub>1.6</sub>	17.8	15.8	17.9	17.0	16.7	14.8
NiCrCoFeMnAl <sub>2.0</sub>	16.9	15.0	17.0	16.0	15.8	19.3

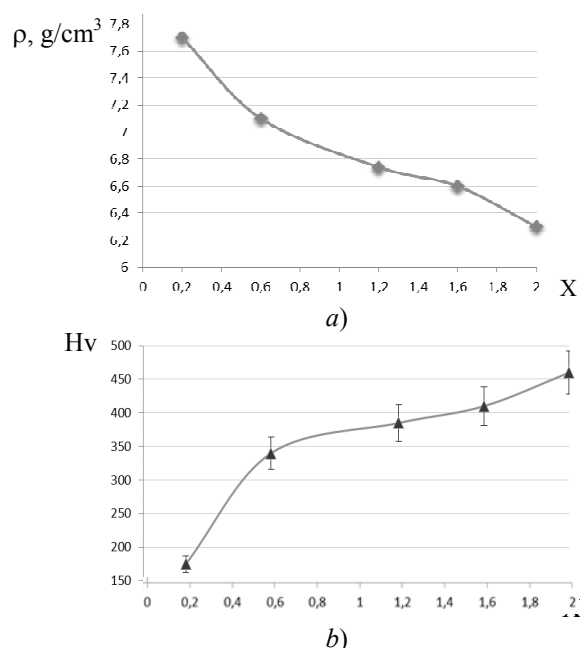


Fig. 1. The influence of the concentration of Al on the density (a) and hardness (b) of alloys

in the alloy contributes to a marked decrease in the density of the synthesized compositions (Fig. 1 a), thus causing a sharp (more than 2-fold) increase in the hardness of the alloys formed (Fig. 1 b).

Such a significant increase in hardness can be explained by the formation of “hard” inclusions of the intermetallic phase, which will be shown below. The results of X-ray phase analysis of synthesized cast HEAs obtained under optimal gravity conditions (150g) showed that the synthesized alloys had a high sensitivity to the concentration of Al on the formation of the phase composition of the HEA (Fig. 2). Thus, at low concentrations ( $x = 0.2$ ), a single-phase product of states is formed from a solid solution with a FCC lattice. Further ( $0.6 \leq x \leq 1.2$ ), a three-phase product consisting of solid solutions with a BCC and FCC lattice and a solid solution based on the  $\beta$ -phase (NiAl-intermetallide) was observed. At  $x \geq 1.6$ , an alloy consisting of a solid solution with a BCC lattice and NiAl intermetallide was formed.

The results of the study of the microstructure of the samples (SEM) of the obtained alloys are shown in Fig. 3 a–d. Acidic etching Fig. 3 a’–d’

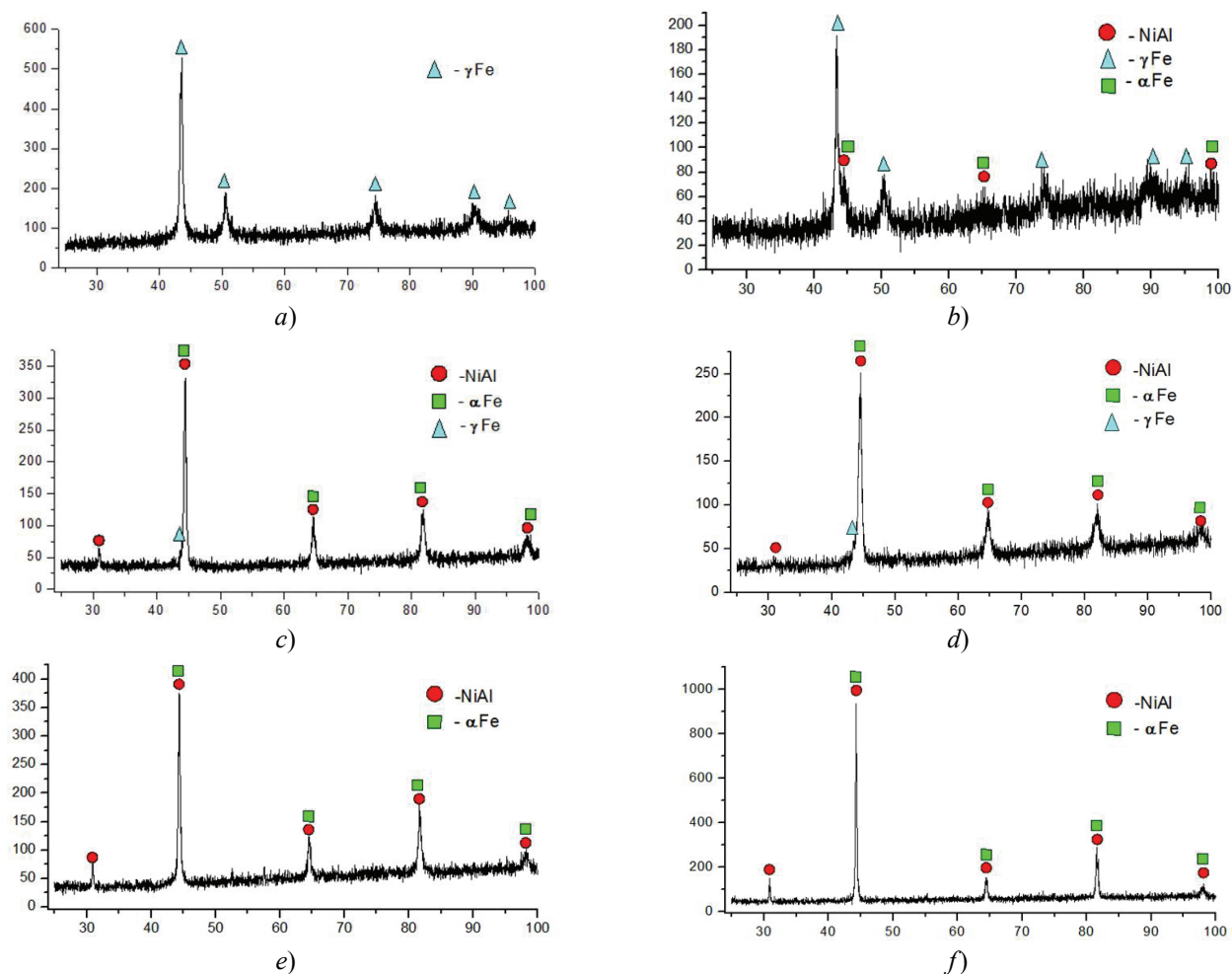
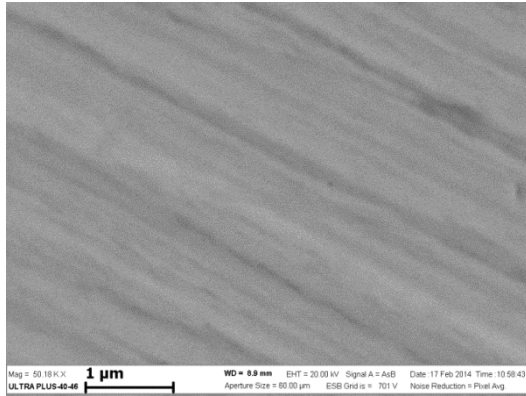
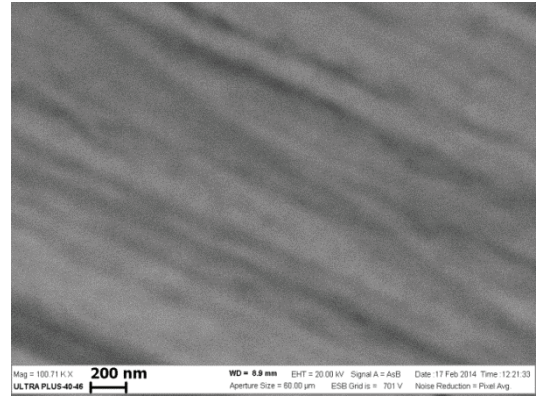


Fig. 2. The results of XRD analysis of NiCrCoFeMnAl<sub>x</sub> alloys:  
a –  $x = 0.2$ ; b –  $x = 0.6$ ; c –  $x = 1.0$ ; d –  $x = 1.2$ ; e –  $x = 1.6$ ; f –  $x = 2.0$

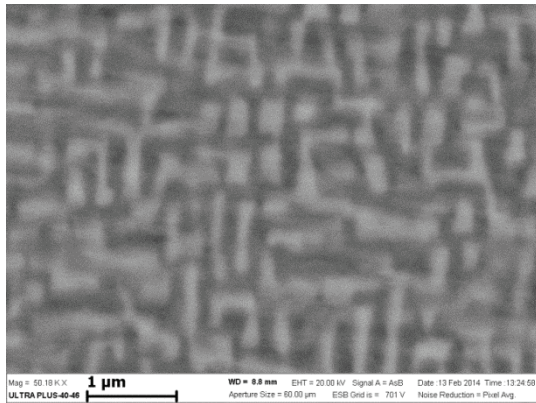




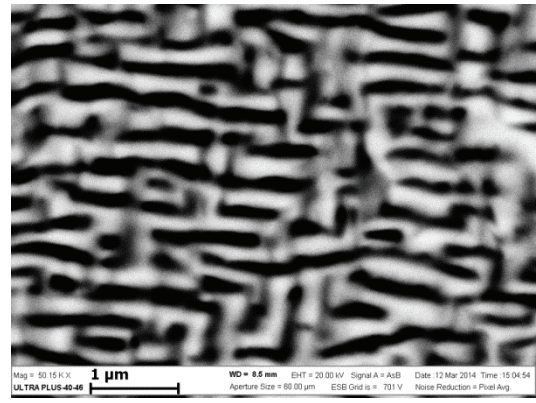
a)



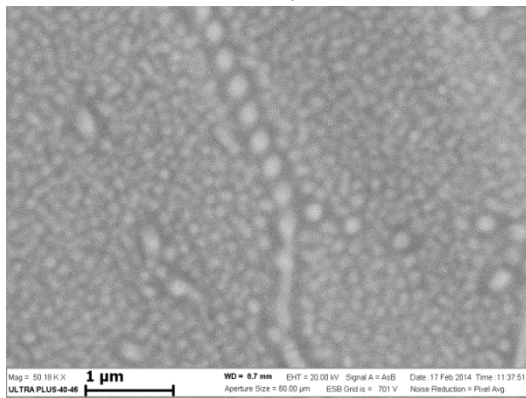
a')



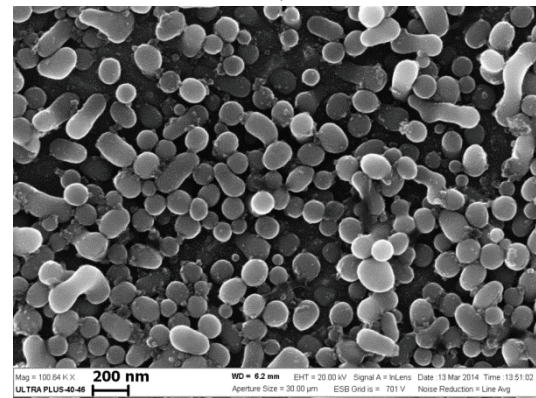
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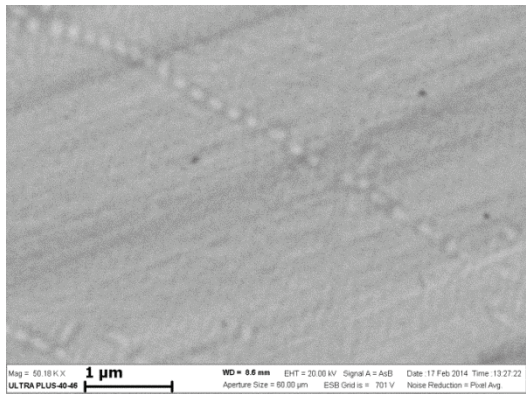
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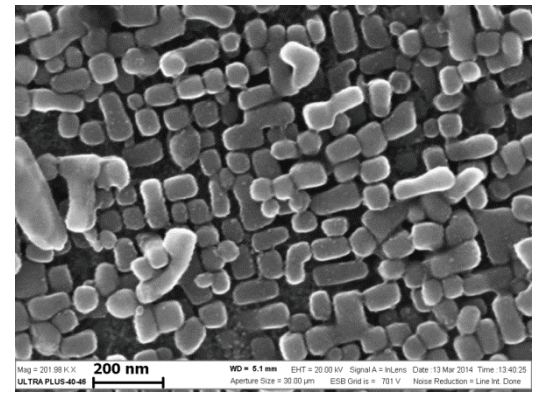
c)



c')



d)



d')

**Fig. 3. The results of the microstructure study (SEM) of NiCrCoFeMnAl<sub>x</sub> alloys:**  
 $a, a' - x = 0.2$ ;  $b, b' - x = 0.6$ ;  $c, c' - x = 1.6$ ;  $d, d' - x = 2.0$ , before and after etching, respectively



of the surface of the samples revealed that alloys with a low Al content ( $x = 0.2$ ) had high resistance to the acidic medium and were single-phase, which agreed with the XRD data. Further, at  $x \geq 0.6$  alloys had a pronounced composite structure. The characteristic size of the dispersion precipitates was 100–150 nm. The shape of the dispersion particles was close to spherical.

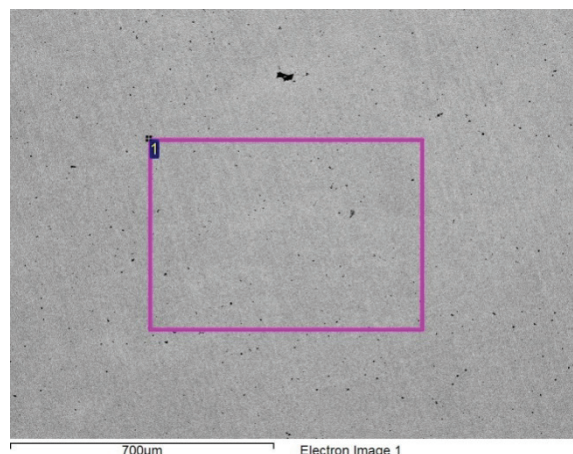
The analysis of the data showed that the obtained alloys had a two-phase composition of a solid solution based on ( $\gamma/\alpha$ -iron) and a solid solution based on the  $\beta$ -phase (NiAl-intermetallide).

The acid treatment of the surface of the samples revealed that alloys had a pronounced composite structure. The size of the structural components was  $\sim 50$ – $100$  nm. The local energy-dispersion analysis of the composition does not allow for measurements with such a scale of structural components.

Therefore, it was of interest to reveal what forms a matrix and dispersion precipitates with a characteristic size of  $\sim 100$  nm. To do this, the samples were subjected to long-term acid etching (more than a day). The results of the analysis of the composition before and after etching are presented in Fig. 4. The analysis of the XRF data and composition of alloys before and after chemical treatment allows us to conclude that the composite structure of the investigated compositions is formed from NiAl as a matrix material, and numerous dispersion precipitates are formed from a solid solution on the bases of Cr and Fe. The revealed structure of alloys can be promising for their use as structural materials of various applications.

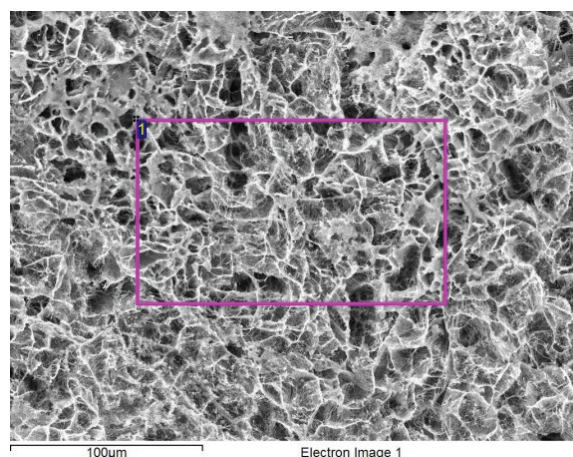
#### *Synthesis of alloys in the Cu–Al–Zr–Ti–(Li–Cr)<sub>x</sub> system*

The formation of alloys based on “lighter” components suggests the use of elements with a low specificity weight. The main difficulty is that most of these elements have a high reactivity and can exert mutual influence on the course of chemical reactions in the combustion wave. It should be noted that there is no practical experience in the formation of such “light” compositions by the methods of SHS-metallurgy. Within this part of the research, special attention was paid to the search and approbation of chemical synthesis schemes for the formation of the materials under study. The two systems were chosen as the model compositions for the study. The chemical scheme for the synthesis of low-density HEAs based on the CuAlZrTi system alloyed with Li and Cr is presented below:



Spectrum	Al	Cr	Mn	Fe	Co	Ni	Total
1	15.0	17.0	13.8	17.2	19.0	18.0	100.00

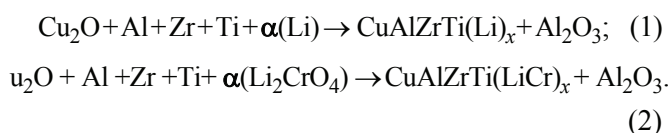
a)



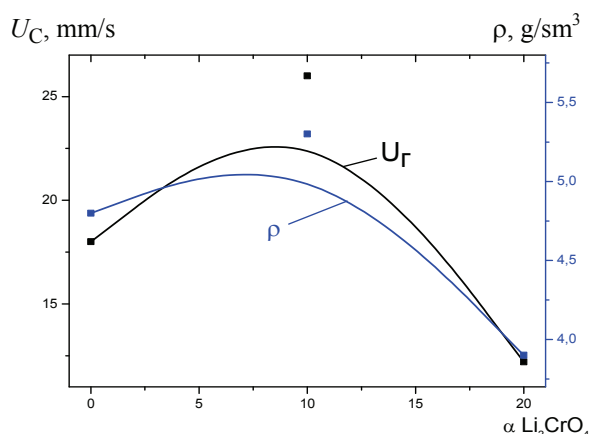
Spectrum	Al	Cr	Mn	Fe	Co	Total
1	1.1	48.7	11.3	31.4	7.5	100.0

b)

**Fig. 4. The microstructure and composition analysis results (EDS) of NiCrCoFeMnAl<sub>1.6</sub> alloy, where (a) is before and (b) is after acidic treatment**



The development of the first composition is based on the introduction of metallic Li. Studies have shown that such a scheme is feasible experimentally and such mixtures are capable of combustion. However, even at overload values of up to 300g, the phase separation in such compositions did not proceed completely due to insufficient combustion temperatures of the compositions, and the analysis of the ingot on the Li content showed a significant difference from the estimated value. We can assume that Li actively takes



**Fig. 5.** The measurement results of the combustion rate ( $U_C$ ) and the density ( $\rho$ ) of synthesized  $\text{CuAlZrTi(LiCr)}_x$  alloys with an increase in the concentration of lithium chromate in the original mixture

part in the reaction of recovery, creating competition to Al. Based on the analysis of the obtained data, it was concluded that the chemical scheme of synthesis (1) was unpromising because it had a small degree of assimilation of Li by the melt.

In the synthesis of the alloy according to scheme (2), Li was introduced into the reaction mixture as a complex oxide ( $\text{Li}_2\text{CrO}_4$ ) preliminarily annealed to dehydrate. The introduction of lithium chromate allowed solving two problems at once: (a) increasing the combustion temperature of the composition as a result of the additional reduction reaction of the complex oxide, (b) increasing the yield of lithium in the alloy due to the fact that Li in the reaction zone was in the bound state at the initial stage. This chemical scheme of synthesis allowed more than double the yield of the target element (Li) in comparison with the scheme (1). Simultaneous introduction of Cr into the composition of the alloy is a positive factor as Cr will increase the resistance of alloys to oxidation.

With a decrease in the specific weight of the metal phase, the problem of separation of the metallic and oxide phases in the SHS process is especially acute. Therefore, all experiments were carried out under the influence of high gravitational fields created in centrifugal SHS plants. Experiments on varying the overload in the range from 50g to 500g revealed that when synthesizing alloys in this system, the optimal interval was 250–300g. Such high values are explained by the fact that the synthesized HEAs had a low specific gravity.

All the ingot samples obtained in accordance with scheme (2) and under optimal conditions (250g) had a molded appearance with a clear separation of oxide (slag) and metal (HEA) phases. Samples were

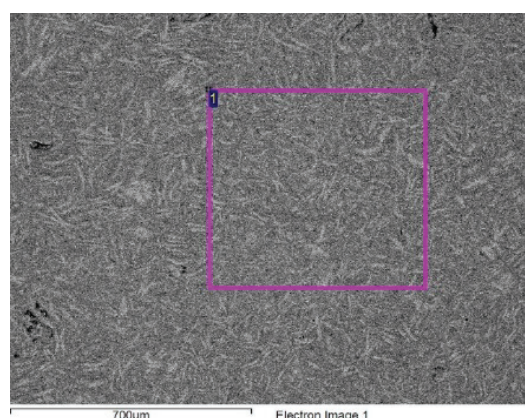
examined by XRF and SEM methods and the alloy density was measured.

The density measurement revealed a nontrivial dependence passing through the maximum. Because the behavior of the density curve of the obtained materials correlates well with the curve for the combustion rate ( $U_C$ ) of the compositions studied.  $U_C$  increased in the first section from 18 mm/s to 26 mm/s, and then decreased to 13 mm/s. It can be assumed that the nonmonotonic nature of the density curve is associated with boiling and volatilization of Li (boiling point 1342 °C). It should be noted that according to the results of the study of this system it was possible to obtain samples of ingots with a density of less than 4 g/cm<sup>3</sup>.

Since the introduced elements can have a strong influence on the formation of the structure, it was of interest to carry out comparative studies of the microstructure of the synthesized alloys. Fig. 6, 7 show the results of microstructure studies using SEM methods and local microanalysis (EDS).

The analysis of the microstructure revealed that in the volume of the alloy there were copper-rich structures. The remaining elements were evenly distributed in the volume of the alloy. It should be noted that such segregation of Cu was previously observed in the works of many authors in the study of the NiCrCoFeCu system [25, 26].

The study of alloyed  $\text{CuAlZrTi(LiCr)}_x$  alloys showed (Fig. 8, 9) that when the Li-Cr additive was added to the alloy composition, the uniformity of the distribution became much higher and the structure was



a)

Spectrum	Al	Ti	Cu	Zr	Total	Spectrum
1	22.00	22.41	35.44	20.15	100.0	1

b)

**Fig. 6.** The microphotograph of (a) structure and microanalysis (b) of the obtained "base"  $\text{CuAlZrTi}$  alloy



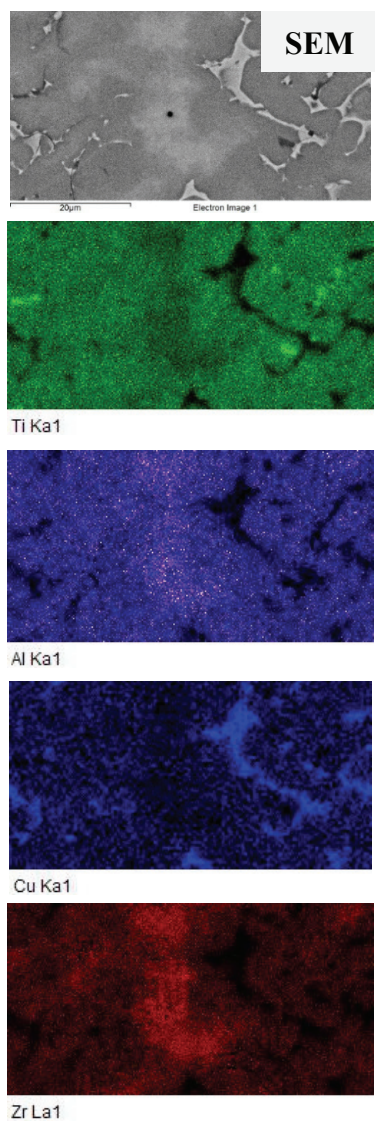


Fig. 7. The map of the distribution of elements (section) for the synthesized “base” CuAlZrTi alloy

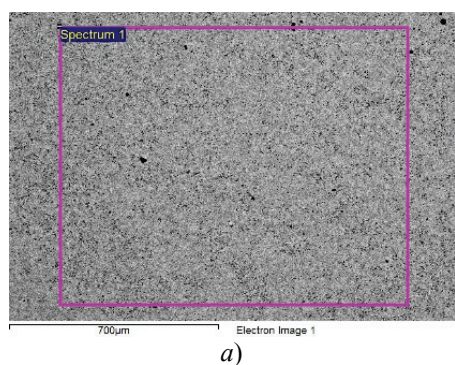


Fig. 8. A micrograph (a) of the structure and microanalysis (b) of the resulting alloy (for the composition of the mixture  $[\text{Cu}_2\text{O} + \text{Al} + \text{Zr} + \text{Ti}] + 20\%(\text{Li}_2\text{CrO}_4)$ )

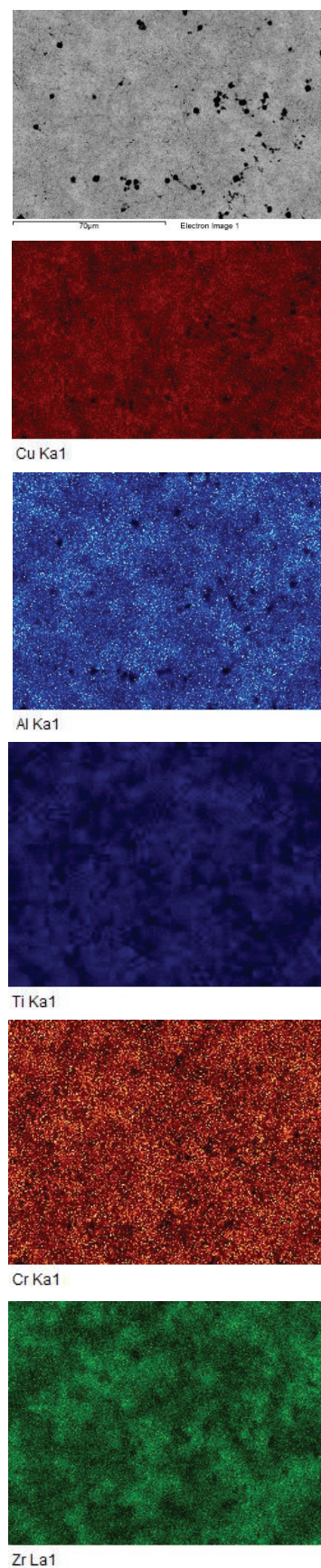
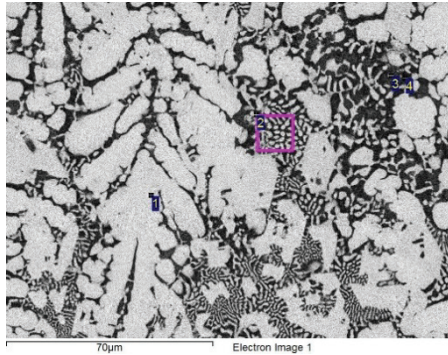


Fig. 9. The map of the distribution of elements (section) for the synthesized  $\text{CuAlZrTi}(\text{LiCr})_x$  alloy





a)

Spectrum	Al	Si	Ti	Cr	Zr	Total
1	23.67	0.00	12.74	12.36	51.22	100.00
2	22.02	0.38	40.89	8.65	28.07	100.00
3	21.16	0.27	61.00	3.72	13.86	100.00
4	23.11	0.14	61.14	8.44	7.17	100.00

b)

**Fig. 10. The microphotograph of (a) structure and microanalysis (b) of the obtained “base” alloy (for the composition of the mixture  $[\text{Cu}_2\text{O} + \text{Al} + \text{Zr} + \text{Ti}] + 30\% (\text{Li}_2\text{CrO}_4)$ )**

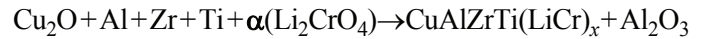
finer-grained. Local segregation of the Cu-rich phase was not observed. Unfortunately, the SEM methods are not suitable for the investigation of Li distribution over the alloy volume because Li is an extremely light element (the 3rd element of the periodic table) and the sensitivity of the method does not allow it to be recorded. However, the analytical research methods (wet chemistry) confirm its presence in the composition of the alloy.

The studies have revealed that with further increase in the concentration of lithium chromate in the composition of the initial mixture leads to a radical change in the structure of the alloy (Fig. 10). As can be seen, the structure of alloys with a high Li content forms large dendrites with an increased content of Zr (point 1). The inter-dendrite space is formed from eutectic colonies enriched with Ti content (point 2).

### Conclusion

The first positive experience in obtaining HEA cast alloys by the SHS-metallurgy was described. The NiCrCoFeMnAlX alloys with a high Al content (up to 15% wt.) were synthesized. A detailed (with greater magnification) analysis of the microstructure of the synthesized alloys revealed that the formed microstructure was multimodal and had hierarchic levels. The most fine-grained precipitates were formed by nano-sized dispersion precipitates in a matrix on the basis of a high-temperature intermetallic NiAl phase.

For the first time, the possibility of forming high-entropy alloys with a low specific gravity using the SHS-metallurgy method was shown. The analysis of the microstructure of the alloy obtained in the



system revealed that the most suitable initial reagent for introducing Li into the composition of the synthesized alloys was complex oxide ( $\text{Li}_2\text{CrO}_4$ ).

The analysis of the obtained data allows drawing a conclusion about the prospects of the materials under investigation and the method of their production for the formation of volumetric nanostructured materials. The production of metallic composite materials based on the new principle of formation of polymetallic alloys can significantly expand the basis for the creation of new materials and facilitate the creation of new technological models.

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