The use of ferroalloys for the smelting of a quasi-high-entropy alloy

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The paper presents the results of studying some properties and structure of a quasi high-entropy alloy (QHEA) of the Co–Cr–Fe–Mn–Ni system melted with the use of ferromanganese and ferrochrome, which presumably will reduce the cost of the alloy.

The paper presents the results of a study of some properties and structure of a quasi-high-entropy alloy of the Co–Cr–Fe–Mn–Ni system, smelted using low-carbon ferromanganese and ferrochrome. The melting was carried out in a laboratory induction furnace with a reinforced cooling system. Casting of the alloy was carried out in a chemically inert corundomullite-zirconium crucible (CMZ), the alloy was subjected to a single remelting to achieve uniformity of composition.

At the end of smelting, the chemical composition, strength, microhardness and some parameters of the experimental alloy structure were studied. The structure of the alloy is represented by a single-phase solution that includes Co, Cr, Fe, Mn, Ni. The content of all the elements is approximately equal (19–22 %) with the exception of iron, whose share is about 15 %. The structure contains a small number of inclusions of silicate nature, the proportion of the total area is about 1%. The experimental alloy demonstrated properties close to the level of properties of a similar alloy melted with the use of pure metals by 5-fold remelting. The results obtained showed the possibility of partial replacement of pure metals with ferroalloys when smelting of QHEAs, which will positively affect their cost. The preliminary calculation shows cost savings on charge materials at the level of 20 %. The results obtained showed the possibility of partial replacement of pure metals with ferroalloys during the smelting of QHEA, which will have a positive effect on their cost.

Key words: quasi-high-entropy alloy, Co–Cr–Fe–Mn–Ni system, ferroalloys, smelting, properties, structure, strength, microhardness, spectrum, entropy.
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Introduction

High-entropy alloys (HEAs) are an updated trend in the development of structural metal materials. The traditional method of smelting a new alloy is to develop a composition based on the main element, with the desired properties achieved through alloying and subsequent processing. As a result of the combined action of these processes, a structure is developed, the basis of which is a matrix with embedded phases of different origin, composition and structure.

When developing a HEA, there is used a completely different principle. The alloy composition contains the minimum of 5 components, preferably in equiatomic concentration or with the content of each element from 35 to 5 %. In this way, a completely different principle of structure formation is implemented, in which there is no basic element forming the matrix. The contribution of each element to the structure formation is comparable with the others and is determined by the composition of the HEA.

The idea of making a HEA is based on the thermodynamic principle of increasing entropy when mixing various components. This process is accompanied by the decreasing of free energy, which increases the likelihood of the formation of simple structures, such as substitutional solid solutions of increased stability. In most HEAs, a single-phase structure of a substitutional solid solution with a simple FCC or BCC lattice is formed [1, 2].

Currently, there is a fairly large number of works that deal with the development of HEAs based on various systems [3–5]. Increased attention to HEAs is determined by the fact that they demonstrate unique properties, such as increased strength, corrosion resistance, wear resistance, cryogenicity, etc. that are significantly superior to similar properties of traditional materials.The uniqueness of the properties is explained by the fact that during the formation of solid solutions of substitution by components with a significant difference in atomic radii, the lattice of the solid solution is greatly distorted, which leads to the improving of a number of properties [6, 7].

Works [7–9] are fundamental studies that review the development, the properties and the structure of various HEAs. The work [8] describes the classical alloy of the Co–Cr–Fe–Mn–Ni system (Cantor's alloy) that showed the promise of using alloys of this system for further research. This study showed that with the basic Co–Cr–Fe–Mn–Ni system, a single-phase solid substitution solution with a FCC lattice is formed. The formation of such a solution determines high strength properties that this alloy demonstrates.

Table 1. Composition of charge materials

Element, % / Material	Mn	Fe	Cr	Ni	Co	C	Si	P	S
FeMn80C05	75.1	25.2	–	–	–	to 0.1	1.85	to 0.3	to 0.03
FH001A	–	32.04	68.2	–	–	to 0.01	0.82	to 0.02	to 0.02
Ni H-1y	–	–	–	99.95		to 0.01	0.002	0.001	0.001
Co K1Ay	0.03	0.2	–	–	99.3	0.02		0.003	0.004

In [8], Cantor established that alloys of the Fe–Cr–Mn–Ni–Co system with equiatomic concentration had a single-phase structure with an FCC lattice. Highly pure metals were used as the charge; high-speed crystallization methods were used during smelting. Subsequent repeated remelting ensured the alloy homogeneity.

Next, the structure was studied by optical, X-ray and electron microscopy. It was found that the structure was a solid single-phase solution of the substitution type.

In a later work [10], the structure of alloys of the Fe–Cr–Ni–Co–X system was studied, where X was understood as Mn, V, Mn and V, Al and Cu. The conducted studies have shown that when alloying the system of this system with the listed elements, two-phase systems of the FCC+ BCC type are already formed or phases of implementation arise.

It should be noted that the common disadvantage of all wind farms is their high cost compared to traditional materials. This is due both to the charge, since weights are smelted from pure metals, and to the peculiarities of smelting, which includes mandatory remelting, accelerated crystallization and other methods to increase the homogeneity of the structure.

The purpose of this work is to study the possibility of smelting a HEA based on the Co–Cr–Fe–Mn–Ni system with partial use of ferroalloys, which will significantly reduce the cost of the alloy.

Ferroalloys are not two-component systems, in any case, depending on the brand, they contain some amount of carbon, silicon, sulfur, phosphorus and other impurities. In this regard, it should be expected that additional phases (possibly introduction phases) will appear in the structure, which are not present in classical wind farms, the structure of which is most often represented by one-two-phase substitution solutions.

For the sake of distinction, we will call the experimental alloy quasi-high-entropy (QHEAs), i.e. pseudo-high-entropy, since the principle of its creation is based on the entropy approach, but the expected structure and method of its production does not correspond to the classical descriptions of HEAs. This technique is widely used in the literature, as an example, the works [11, 12] can be cited.

Materials and methods

The following charge materials were used for smelting: ferromanganese grade FeMn80C05 (GOST 4755-91), ferrochrome grade FH001A GOST 4757-91, grade N-1u (SS 849-97) metallic nickel and grade K1Au (SS 123-2008) metallic cobalt. The chemical composition of the charge materials is given in **Table 1**. The content of the main elements was determined using a Niton spectrometer, the values of the remaining elements are indicated in accordance with SS.

The composition of the charge was selected in such a way that the share of each component in the final alloy would be about 20 %.

The dispersion of all the components was 90 % represented by the fraction of 3–5 mm. Next, the charge mixture was thoroughly mixed and smelted in a UIP-16-10-0.005(Fe)-UHL4 laboratory furnace with an enhanced cooling system. To achieve a uniform composition and to eliminate external contamination, the resulting ingot (weight 0.9 kg) was poured into a chemically inert corundomullito zirconium crucible (CMZ), remelted and then poured back into the CMZ crucible. After complete cooling, samples were prepared from the ingot for analysis. The chemical composition, microhardness, strength and structure were studied.

The chemical composition of the test ingot was determined using a Poly Spec-F spectrometer. To study the fine structure of the prototypes, a TESCAN VEGA scanning electron microscope equipped with an X-ray energy-dispersive spectrometer was used.

X-ray studies were carried out on an X'PertPRO diffractometer using CuK_{α}-radiation. The experimental spectra were processed using the diffractometer software: X'Pert High Score Plusversion 2.2b and X'Pert High Score version 2.2b.

Microhardness was determined using a Willson 1150 instrument; measurements were taken at no less than 5 points. Tensile strength was determined on an INSTRON testing machine with 3 takes. Thixomet Pro software was used to analyze the structure, which allows for various types of quantitative metallographic analysis.

Results and discussion

Table 2 presents the results of the chemical analysis of the experimental ingot. The characteristics of the alloy indicated in [7] were used as a comparison (reference) sample. The alloy specified in [7] belongs to the HEAs class and was obtained by electric arc melting of pure metals followed by casting into a water-cooled copper mold. To ensure chemical uniformity, the ingot was melted at least 5 times. It is seen from the data in Table 2 that the composition of the experimental alloy does not correspond to the equiatomic composition, although it can be classified as a quasi high-entropy alloy, because the content of each element does not exceed 35 % but is larger than 5 %.

A rather low Fe content in the experimental alloy is due to its low content in ferromanganese, because grade FeMn80C05 ferromanganese was used. The use of ferromanganese with a higher iron content is not considered

Table 2. Chemical composition of the obtained ingot

No.	Element, %	Fe	Cr	Mn	Co	Ni	Si+ res
1	Experimental	15.3	23.3	22.4	19.1	19.2	0.70
2	Comparison (reference) alloy	20.06	19.87	19.46	19.87	19.97	0.77

in this case, because such grades contain a high percentage of carbon (about 7%), which is undesirable in this study.

If we carry out the simplest calculation of the entropy of the alloy according to the formula:

$$\Delta S = R\sum_i^n C_i lnC_i ,$$

where: R – the universal gas constant

C_i – the concentration of the i-element,

then we get the following values: for the comparison alloy, the enthalpy of mixing is $\Delta S = 2511.86 \frac{J}{mol * K}$;

for the experimental alloy, this value is $2474,21 \frac{J}{mol * K}$.

While for steel grade 1Kh18N9T, the value of the enthalpy of mixing is only $596.59 \frac{J}{mol * K}$. These values allow us to classify the smelted alloy as a class of high-entropy alloys and expect from the alloy characteristics close to the corresponding parameters of the approximate composition of the HEAs. For this purpose, an analysis of the microhardness and strength of the experimental alloy was carried out. **Table 3** shows similar characteristics of the comparison alloy for comparison.

Table 3. Microhardness and strength of the samples

Sample	Microhardness, HV	Ultimate strength, MPA	Grain average diameter, μm
Experimental	130	430	183
Reference (comparison) alloy	136	443	180

The data in Table 3 show that the experimental alloy is not inferior to the comparison sample in terms of the specified characteristics.

Fig. 1 shows the structure of the experimental alloy and the results of MRSA at 4 points. It can be seen from the data in **Table 4** and the given characteristic spectrum that the structure contains Fe, Cr, Mn, Co and Ni, and their concentration practically coincides with the concentration of elements obtained on Poly Spec-F. The matrix also contains minor inclusions, presumably of silicate nature. Table 4 shows concentrations of chemical elements in the selected spectra.

Table 4. Chemical elements concentrations expressed in weight percent

Spectra	Element content in the selected spectrum, wt. %					
	Ni	Cr	Fe	Mn	Co	Si
1	18.9	23.1	15.3	21.43	18.9	–
2	19.32	23.2	14.87	22.13	19.21	–
3	19.21	22.98	15.02	22.31	19.5	-
4	19.28	22.30	15.2	22.48	19.6	–
5	–	–	–	–	–	0.9

Spectrum 5 (inclusion) differs in composition from the other spectra; the only one of the spectra contains silicon in the complete absence of other elements. Analysis of the inclusion (**Fig. 2**) showed that the inclusion appears to be of silicate nature; its genesis is associated with the presence of silicon in the charge materials.

Inclusions of silicate type are undesirable in the matrix, because they disrupt its homogeneity and can play the role of a glassy phase, which reduces the plasticity of the matrix.

X-ray phase analysis was performed to identify the phase composition of the studied samples. The X-ray images obtained are shown in **Fig. 3**. **Table 5** shows the results of semi-quantitative X-ray phase analysis of crystalline phases.

Comparative analysis of the obtained X-ray images of the prototypes (Table 5) confirmed the chemical analysis data (Table 4). A slight difference in the content of the main elements from 100 % indicates the presence of impurities (inclusions).

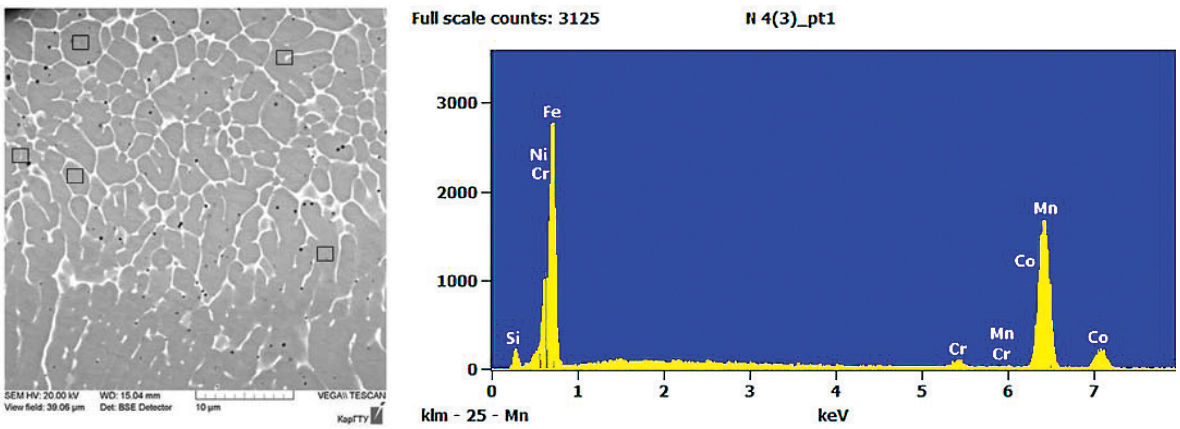

Fig. 1. The characteristic spectrum of the experimental alloy

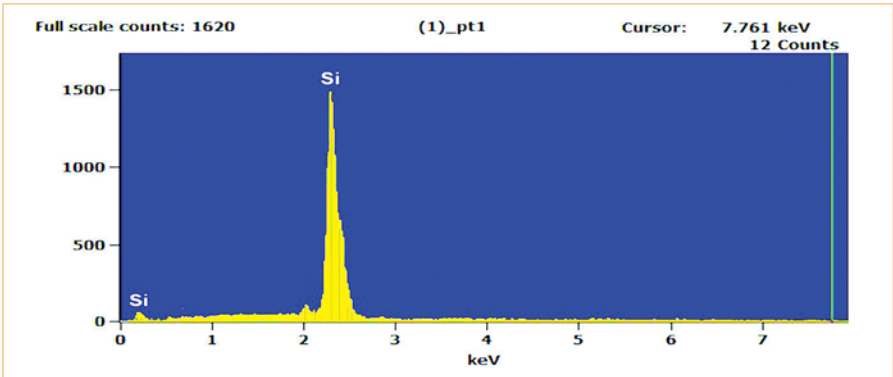

Fig. 2. Inclusion characteristic spectrum

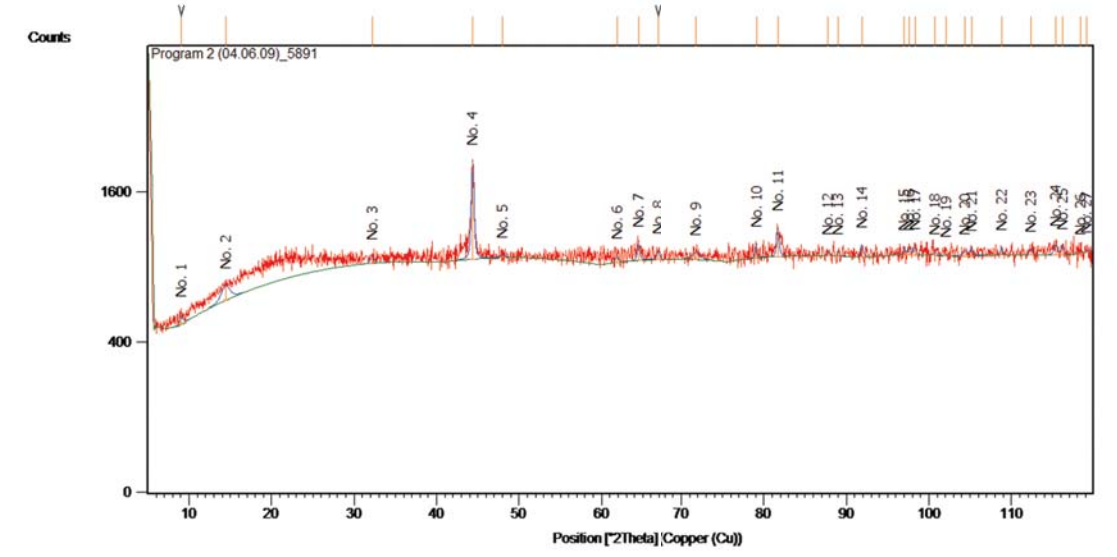

Fig. 3. Diffraction pattern of the experimental alloy

Table 5. Results of semi-quantitative X-ray phase analysis of crystalline phases

No.	Interplane distance, A°	Peak intensity, %	Element	Chemical symbol	Concentration, %
1	6.1391	10.69	Iron	Fe	16.02
2	2.77961	5.41	Chromium	Cr	23.5
3	2.03977	100	Nickel	Ni	19.1
4	1.89408	2.5	Manganese	Mn	22.03
5	1.44355	14.8	Cobalt	Co	19.1

To determine the possible risks associated with the presence of inclusions, a quantitative analysis of the main characteristics of inclusions was carried out.

Quantitative characteristics of inclusions were obtained using Thixomet Pro software. 15 fields of view were analyzed, the number of objects in each of the fields of view ranged from 12 to 21, the average number of objects in the field of view is 14.

The following quantitative characteristics were obtained:

– the average value of the inclusion area is 4.42 mm^2;

– the average value of the perimeter of inclusions is 8.58 μm;

– the average value of the diameter of inclusions is 2.61 μm;

– the total area occupied by inclusions is 1.1 %.

The data show that the inclusions have a fairly spherical shape (the shape factor is close to 1), are quite small (the average area value is 4.42 μm^2) and occupy in general a fairly small area, about 1 % of the total area of the field of view.

Having analyzed such quantities as the calculated entropy of mixing, microhardness and strength of the experimental alloy in comparison with similar characteristics of a high-entropy alloy based on a similar Co–Cr–Fe–Mn–Ni system, it can be argued that the experimental alloy can be classified as a HEAs. However, given that the equiatomic concentration has not been reached in the experimental alloy, and there is also a certain amount of the embedding phase in the form of silicate inclusions, this alloy can be characterized as quasi-high-entropy (pseudo-high-entropy).

It should be expected that the partial use of ferroalloys instead of pure metals will reduce the cost of the alloy. For this purpose, the cost of an alloy made from pure metals

and an experimental alloy made using ferromanganese and ferrochromium was calculated, while only the cost of charge materials per 1 kg was taken into account according to the average market price in the territory of the Republic of Kazakhstan.

An approximate calculation shows that the cost of the charge for smelting an alloy of pure metals is approximately 233 CU.

Thus, savings due to charge materials of about 20 % are provided, provided that all other smelting parameters remain the same. With a conditional serial production of 100,000 pcs/year of parts weighing 0.3 kg, the cost savings will be approximately 1.4 million units.

The conducted studies on the smelting of QHEAs with partial use of ferroalloys instead of pure metals have shown the fundamental possibility of such a replacement. In this work, the replacement rate was 40 % (2 out of 5 components). The expansion of the basic system, for example, to 6 components, will increase the proportion of replacement ferroalloys to 50 %, which, accordingly, will increase the concentration of iron in the alloy and will allow to obtain a composition even closer to the equiatomic concentration. In addition, the use of ferroalloys in the smelting of QHEAs provides broad prospects for creating certain properties, for example, corrosion resistance, provided that ferroalloys containing an element of the desired nature are used.

Conclusion

As a result of the studies, the possibility of smelting QHEAs based on the Co–Cr–Fe–Mn–Ni system with partial replacement of pure metals with ferroalloys was established. The properties of the experimental alloy are similar to those of QHEAs based on a similar system but smelted with the use of pure metals with a 5-fold remelting. The results obtained showed that despite the appearance of a small amount of silicate phase in the structure (about 1 % of the total area of the strip) and the presence of some impurities in the initial charge, the properties of the experimental alloy are comparable to those of an alloy made from pure metals.

The conducted studies have shown the possibility of partial replacement of pure metals with ferroalloys during the smelting of a high-entropy alloy, which will have a positive effect on their cost. The preliminary calculation shows cost savings on charge materials at the level of 20 %. This suggests that the experimental alloy will be attractive for further research in order to improve its properties for industrial use.

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