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RESEARCH PAPER

The molybdenum effect on the structure and properties of the quasi-high-entropy alloy of the Fe-Co-Cr-Ni-Mn-Nb system

Svetlana Sergeevna Kvon[1], Vitaly Yurievich Kulikov[1], Aristotel Zeinullinovich Issagulov[1], Tatyana Victorovna Kovalyova[1], Aizhan Rymkulkyzy Abildina[1]*

[1] Abylkas Saginov Karaganda Technical University, Department of Nanotechnology and Metallurgy, Nursultan Nazarbayev Avenue No. 56, 100003, Karaganda, Kazakhstan

*Corresponding author: t.kovalyova@ktu.edu.kz, tel.: +77076233742, Department of Nanotechnology and Metallurgy, Abylkas Saginov Karaganda Technical University, Nursultan Nazarbayev Avenue No. 56, 100003, Karaganda, Kazakhstan

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ABSTRACT

The results of the study of the effect of molybdenum on the structure and properties of the quasi-high-entropy alloy (QHEA) of the Fe-Co-Cr-Ni-Mn-Nb system are presented in this paper. Together with pure metals, ferroalloys were also used in smelting experimental alloys. Due to pure metals and ferroalloys, the obtained experimental alloys were called QHEA in contrast to HEA (high-entropy alloys). It was found that solid solutions of the FCC type (Mn, Fe, Co, Ni) and ICC type (Nb, Mo), σ-phase (Cr, Mo), carbides Cr_3C_7, (Nb, Mo)C and Laves phases (Nb, Mo)(Fe, Ni, Mn)2 were formed in the final structure of the studied samples. For the first time, the presence of such phases as carbides Cr_3C_7 and (Nb,Mo)C was established in the alloy structure, which were not described in similar studies devoted to the effect of molybdenum on the properties of alloys of the Fe-Co-Cr-Ni-Mn-Nb system. Adding Mo in 5-15% by weight increased the hardness from 243 HV to 689 HV and the strength from 550 MPa to 980 MPa without changing the ductility values.

Keywords: quasi high-entropy alloy, Fe-Co-Cr-Ni-Mn-Nb system, molybdenum, structure, properties, solid solution, carbides

INTRODUCTION

A single basic element usually forms the structure of most alloys. This basic element forms a matrix. Alloying and subsequent treatment form new phases that dictate the required properties. The creation of high-entropy alloys (HEAs) is carried out on a different principle: the main element is absent and all elements (at least 5) have the same probability of occupying the nodes of the crystal lattice. **Fig. 1** illustrates the difference in the arrangement of atoms (A, B, C, D, E, F are atoms of different metals) in pure metal, classical alloy, and HEA.

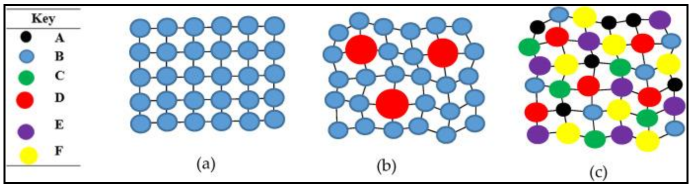

Fig. 1 Diagram of the structures of a pure metal (a), a classical alloy (b) and a high-entropy alloy (c) [1]

The five-component alloy of the Co-Cr-Fe-Ni-Mn system, the so-called Cantor alloy, is one of the first well-studied HEAs [2]. The Cantor alloy has high mechanical properties: tensile strength of 491 MPa and yield strength of 292 MPa. At the same time, relative elongation can reach 50%. High values of strength and plasticity are a unique combination that cannot be achieved, for example, in steels or other classic alloys [2-3].

A large number of studies have been carried out to improve the mechanical properties of the Cantor alloy, in particular strength, since the value of the existing strength indicator is insufficient for creating high-strength structures or products.

Research [2-9] studies the influence of various elements on the strength and hardness of Co-Cr-Fe-Ni-Mn alloys. Elements such as Ti, Nb, Mo, B, and Si were used as the sixth element in the Cantor alloy. The influence of molybdenum as an extra element in the Cantor alloy was studied in [11-14]. The increased interest of researchers in such an element as molybdenum is explained by the fact that molybdenum atoms have a large diameter. The diameter of the Molybdenum atom is 0.280 nm (for comparison, the diameter of the Iron atom is 0.254 nm). This leads to a significant distortion of the crystal lattice of the alloy and, consequently, to strengthening.

In addition, molybdenum has a positive effect on reducing temper brittleness, which makes it an essentially "mandatory element" in hardened steels. It is logical to assume that molybdenum has the same positive effect on temper brittleness in HEAs.

In [11], a study was conducted on the influence of molybdenum on the mechanical characteristics of the Fe-Cr-Co-Ni system of HEA. The high-entropy alloys had high plasticity and low strength. The introduction of molybdenum from approximately 2 to 6 mass% % led to the formation of intermetallics of the σ- and μ-phase type, enriched with Mo. The formation of these brittle but very hard phases located in the viscous matrix of the FCC solution led to an increase in the strength of the alloy. The tensile strength reached up to 1.2 GPa, and the ductility was 19%. This study showed the possibility of increasing the strength of the HEA due to the formation of brittle but hard phases in the viscous matrix, without reducing the plasticity of the alloy. The authors of [11] explained that transitioning from a dendritic structure with an FCC lattice to a combination of FCC+BCC+σ-structure increased the strength. The strengthening was the result of the precipitation of the BCC and σ-phases. The researchers concluded that significant strengthening resulted from separating the BCC and σ-phases in that case.

In study [12], the authors carried out an experimental assessment of the possibility of synthesising a HEA with a base (Co-Cr-Fe-Ni-Mn) enriched with borides and silicides of Mo and Nb, which were formed during the thermite combustion of SHS systems. The microstructural analysis of the Co-Cr-Fe-Ni-Mn alloy with a complex additive of Mo(Nb)-Si-B showed that with increasing concentration of the additive, high-entropy matrices were formed in the structure, and new phases based on borides and silicides (Mo and Nb) were formed.

In [13], a new fine-structured high-entropy alloy CrFeNiAl0.27Si0.11Mo0.22 obtained by arc melting was proposed. The experimental alloys had high mechanical properties: tensile strength ≥1GPa and ductility ≈15.5%. This alloy also had excellent corrosion resistance in the 3.5% NaCl medium due to forming a thin molybdenum oxide film.

In the study [14], the authors developed a new alloy FeCoCrNiMoSix with different Si content following the atomic ratio Fe:Co:Cr:Ni:Mo:Si = 1:1:1:1:1:x (where x=0.5;1.0;1.5). Mo's positive effect on the alloys' strength properties was noted. However, the positive effect of silicon was observed.

It should be noted that the common disadvantage of all the listed high-entropy alloys is their high cost compared to traditional materials.

The composition of the charge and the alloy smelting features increase the cost of HEAs. Thus, the charge must contain only pure metals. The smelting process

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consists of multiple mandatory remelting, plasma synthesis, accelerated crystallisation, and other methods of increasing the homogeneity of the structure.

The creation of so-called quasi-high-entropy alloys (QHEA) is a popular way to reduce the cost of producing alloys [15,16].

The general principle of QHEAs production is the same as HEAs: a multi-component system consisting of at least 5 components is used, while the main element that forms the alloy matrix is missing. The equiatomic concentration is not strictly observed in QHEAs. Additionally, the charge and production method requirements are significantly lower in QHEAs production. This makes it possible to increase the commercial attractiveness of QHEAs with a level of properties comparable to those of HEAs.

In work [16], studies of the Fe-Cr-Mn-Ni-Co-Nb system were carried out. The alloy was obtained with the partial use of ferroalloys. The results showed the possibility of obtaining alloys partially replacing pure metals with corresponding ferroalloys. The obtained samples corresponded to the principles of the VES. The technology of alloy production was simpler, which determined the lower cost.

This work aims to investigate the effect of different molybdenum contents on the structure and mechanical properties of the Fe-Cr-Mn-Ni-Co-Nb system. It is obvious that partial use of ferroalloys in the charge, which additionally contain C, Si and some other elements, will lead to changes in the structure and the formation of new phases that have not been described in the previous scientific studies related to the effect of molybdenum on the properties of Fe-Co-Cr-Ni-Mn-Nb system alloys.

MATERIAL AND METHODS

Ferromanganese grade FeMn80C05, ferrochrome grade FK005, ferroniobium grade FNb60, nickel cathode grade Ni-1u, metallic cobalt grade Co1Au and ferromolybdenum grade FMo60 were used as charge materials. **Table 1** shows the chemical composition of the charge components.

The composition of the charge was calculated in such a way that the Mo content was equal to 5, 10, 15 mass %, the Nb content was equal to about 14% by weight, and the content of the remaining elements was approximately in equal proportions.

Ferroalloys were ground in a mill from an initial size of 50-100 mm to a fraction of 2-3 mm for better melting. The volume of the grinding cup was 50 ml; the diameter of the grinding balls was 12 mm in the amount of 6 pcs. The grinding balls were made of tungsten carbide, and the cup was made of stainless steel. The rotation speed was 1000 rpm.

The components' dispersion was 90% represented by the fraction of 2-3 mm. The fractional composition of the materials was determined using an analytical sieving machine AS 200 control (Retsch, Germany). The charge mixture was stirred in a laboratory Schatz mixer for 15 minutes. The charge mixture was melted in an induction furnace model UIP-0.5 with an enhanced cooling system in an air atmosphere. After melting, the liquid melt was poured into alundum crucibles. The alloy was cooled in a calm state at room temperature. Then the solidified alloy was remelted again in the furnace. The melt was poured into alundum crucibles. Re-melting was carried out to homogenize the structure and eliminate liquation in the volume of the ingot metal.

After complete cooling, samples were prepared from the ingot for analysis. The experimental samples were studied for chemical composition, hardness, compressive strength, plasticity (relative elongation), and structure. The chemical composition was determined using a Poly Spec-F spectrometer (Italy).

The structure was analyzed using an S-3400N scanning electron microscope with a NORAN X-ray energy-dispersive spectrometer from the Hitachi High Technologies Corporation.

ThermoCalc software (TCFE13 database) was used for the modelling. The program contains information on 435 phases and considers oxygen-nitrogen conditions for the stability analysis of the alloy components. The study was performed in the temperature range from 500 to 1600 °C to obtain the most complete picture of the phase changes.

Hardness was determined on a Willson 1150 device with a load of 50 kgf. Five measurements were taken randomly, with the calculation of the arithmetic mean.

The tensile strength was determined on an INSTRON testing machine with three duplicates.

Relative elongation was calculated automatically using the INSTRON testing machine software. It can also be calculated using the following formula (1):

$$f = \frac{l_f}{l_0} 100\% \qquad (1)$$

where l_f – it is the final length of the sample, [mm];
l_o - it is the initial length of the sample, [mm].

X-ray phase analysis was performed on a Bruker D2Phaser X-ray diffractometer with a Siemens KFL-CU-2K Cu–2K X-ray tube (copper anode). The DIFFRAC.EVA and DIFFRAC.TOPAS programs were used to identify and quantitatively calculate phase content.

Table 1 The charge material composition

Material element, mass %	**FeMn80C05**	**FK005**	**FNb60**	**Ni -1u**	**Co1Au**	**FMo60**
Mn	75.1	-	-	-	0.03	-
Nb	-	-	62	-	-	-
Fe	25.2	32.04	35.50	-	0.2	38.8
Cr	-	68.2	-	-	-	-
Ni	-	-	-	99.95	-	-
Co	-	-	-	-	99.3	-
Mo	-	-	-	-	-	60.2
C	0.1	0.01	0.3	0.01	0.02	0.08
Si	1.85	0.82	1.8	0.002	-	0.8
P	up to 0.3	up to 0.02	0.04	0.001	0.003	0.05
S	up to 0.03	up to 0.02	0.05	0.001	0.004	0.01

RESULTS AND DISCUSSION

Fig. 2 shows the phase equilibrium diagram for the Fe-Cr-Ni-Co-Mn-Nb-Mo system, which was obtained using ThermoCalc software. The composition with the Mo content of more than 15 mass % was not studied, since preliminary melts showed that even after 3 remelts, undissolved ferromolybdenum particles remained in the sample.

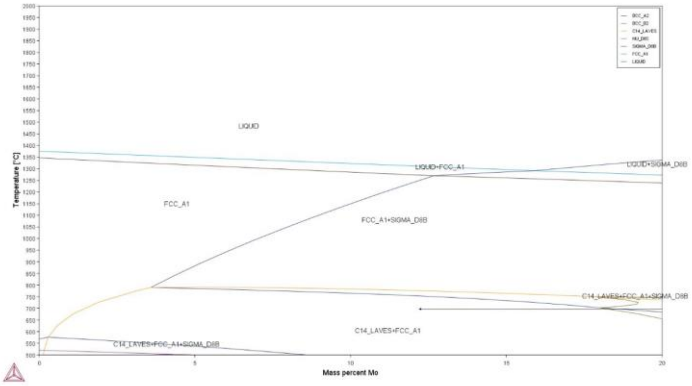


Fig. 2 Equilibrium phase diagram of the Fe-Cr-Mn-Ni-Co-Nb system

The diagram (**Fig. 2**) shows that the expected phases in the alloys are the FCC-type solid solution, σ-phase, and Laves phase. The σ-phase is characterized as an intermetallic compound with a high content of Cr and Mo [11]. It should be noted that elements such as C and Si were not taken into account in this calculation, although C and Si are present in the initial charge as part of ferroalloys and affect the formation of phases.

Table 3 shows that the hardness of the samples increased with increasing molybdenum content. With the addition of molybdenum in the amount of 5% by weight (sample No. 1), the hardness of the sample increased almost 2 times (482 HV) compared to sample No. 0 (243 HV, without Mo). The hardness values of the samples continued to grow with increasing molybdenum content: 639 HV (sample No. 2), 689 HV (sample No. 3).

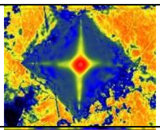
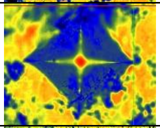
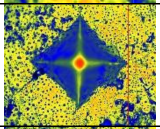
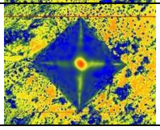
Table 2 Chemical composition of the samples under study

Sample/ element, mass %	0	1	2	3
Co	16.94	15.64	14.12	13.29
Cr	16.82	15.67	14.84	13.127
Fe	18.50	18.02	17.95	17.42
Ni	16.73	16.02	14.28	13.08
Mn	16.53	15.28	15.15	14.52
Nb	14.23	14.20	14.33	14.02
C	0.23	0.28	0.28	0.29
Mo	-	4.86	9.05	14.25
Si	0.002	0.003	0.002	0.003
P	trace	trace	trace	trace
S	trace	trace	trace	trace

A similar trend is observed when determining the compressive strength (**Table 3**): 550 MPa (without Mo, sample No. 0); 720 MPa (5 mass %. Mo, sample No. 1), 940 MPa (10 mass % Mo, sample No. 2); 980 MPa (15 mass % Mo, sample No. 3). It should be noted that the plasticity of the samples remained virtually unchanged.

In works [11, 13], the same phenomenon was observed: a significant increase in the ultimate strength while maintaining the samples' high plasticity. The authors explained this fact by forming a mixture of FCC and ICC solid solutions and the presence of brittle but extremely hard σ and μ-phases in the structure.

Table 3 Mechanical properties of the samples under study

Sample No.	Test result	Hardness, HV	Compressive strength, MPa	Relative elongation, %
0		243	550	19.1
1		482	720	18.8
2		639	940	18.5
3		689	980	18.4

Ferroalloys and pure metals were used as charge components in our work. Therefore, the presence of carbon in the melt is possible since ferroalloys were used. The presence of carbon in the melt ensures the formation of carbide phases. The increased hardness and compressive strength was likely due to the formation of additional phases different from the σ and μ-phases noted in [11, 13]. To verify this assumption, the structures of the experimental samples were studied (**Fig. 3**).

Fig. 4–6 illustrates the distribution maps of elements in the structure of the experimental samples. We observed at least 4 different zones in all the samples studied: light, gray, dark gray and interstitial phases. It is logical to assume that the lighter areas of the structure contain a greater amount of heavy elements, in this case, Mo and Nb.

The element distribution map (**Fig. 4**) shows that elements such as Mn, Ni, Co, and Fe are distributed uniformly in sample No. 1. These elements form a solid solution of the FCC type, which is consistent with the calculated diagram (**Fig. 2**). The distribution of elements such as Cr, Nb, and Mo is extremely uneven, with Nb and Mo elements present in one zone and Cr located in the surrounding zones.

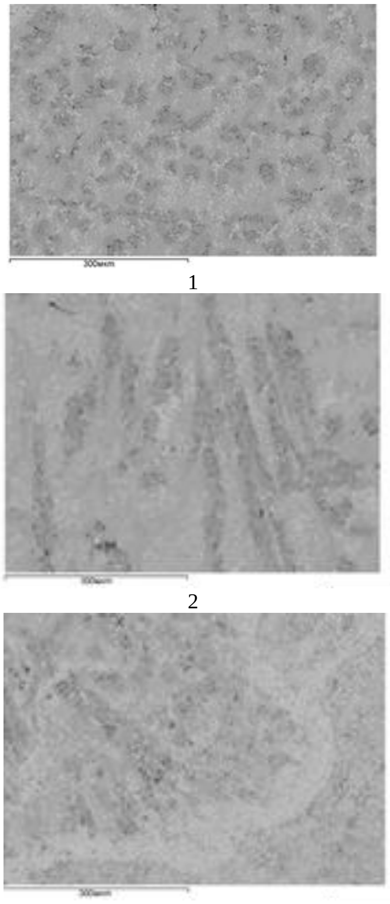

1
2
3

Fig. 3 The structures of experimental samples: the figure indicates the sample number (**Table 2**)

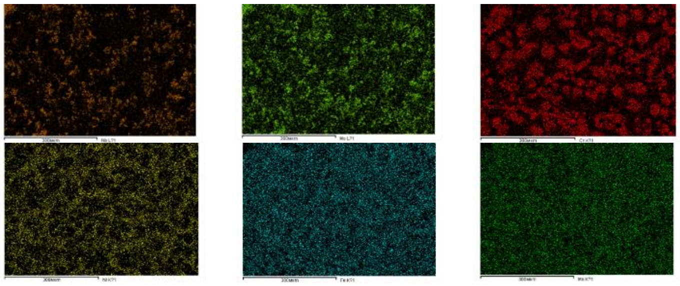


Fig. 4 Distribution map of elements in sample No. 1

Fig. 5 shows the distribution map of elements in the structure of sample No. 2.

In the structure of sample No. 2, approximately the same picture is observed. Fe, Mn, Co, Ni are distributed uniformly, forming a solid solution presumably of the FCC type. Nb and Mo are localized in another zone, creating a solution presumably of the ICC type. Cr is also distributed unevenly, localizing in darker zones where interstitial phases are also observed.

The distribution map of elements in the structure of sample No. 3 is approximately the same as in samples No. 1 and No. 2 (**Fig. 6**): Fe, Mn, Co, Ni are distributed uniformly, Nb and Mo are localized together and form the lightest zone in the structure, Cr is observed in darker zones, where interstitial phases are also present.

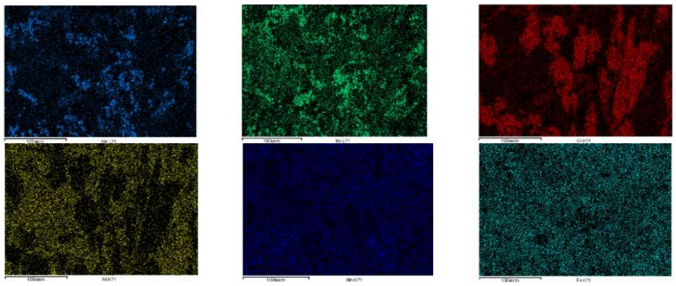


Fig. 5 Distribution map of elements in sample No. 2

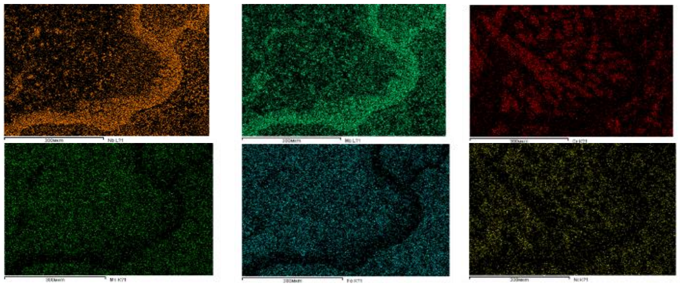


Fig. 6 Distribution map of elements in sample No. 2

Based on the analysis of the element distribution maps in the sample structures, it can be assumed that Fe, Mn, Co, Ni form a solid solution of the FCC type. Nb and Mo form another solid solution of the ICC type, which agrees with the calculated phase equilibrium diagram and the crystal lattices of the elements themselves. **Fig. 7** illustrates the X-ray diffraction pattern of sample No. 3, as the most typical among the samples studied.

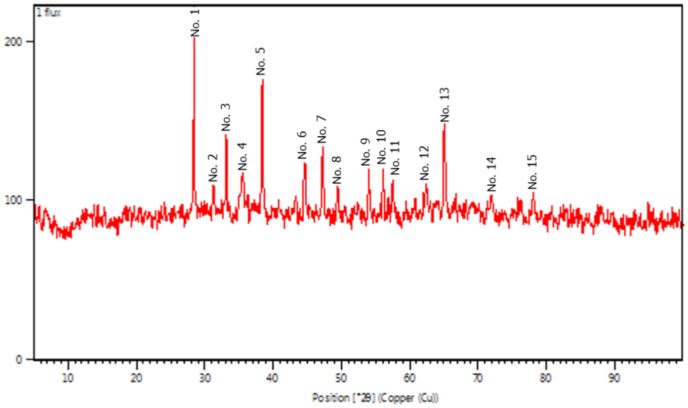


Fig. 7 X-ray diffraction pattern of sample No. 3

The calculations show that, as expected, FCC-ICC solutions, σ-phases, NbC, cementite-type carbides and Laves phases are present in the structure. A selective MRSA (**Table 4**) confirmed the presence of these phases in the structure (**Fig. 8**). The data in **Table 4** demonstrate that the elemental composition of the spectra corresponds to the composition of the solid solution. Spectra 76, 77, and 82 contain approximately the same content of Mn, Fe, Co, and Ni and are depleted in Nb and Mo. Therefore, they can be interpreted as a solid solution of these elements of the FCC type.

Spectrum 75, on the contrary, contains an increased content of Nb and Mo, consistent with their mutual solubility and the ability to form a solid solution of the ICC type.

Spectrum 78 contains a large amount of Cr and Mo, which is interpreted in [11, 14] as the σ-phase. Unfortunately, this study was unable to observe the μ-phase, which is mentioned in [11].

Table 4 Results of semi-quantitative X-ray phase analysis

No	1	3	5	6	7	13
d-spacing [nm]	0,33417	0,18184	0,10150	0,71653	0,42563	0,15419
Rel. Int. [%]	100	34,34	27,48	12,53	19,65	18,85
Compound Name	Manganese Iron Cobalt	Niobium Molybdenum	Chromium Carbide	Sigma	Niobium Molybdenum Carbide	Laves
Chemical Formula	FCC (Mn,Fe, Co)	ICC (Nb,Mo)	Cr_3C_7	σ	(Nb,Mo) C	AB_2
SemiQuant [%]	43	14	17	8	11	7

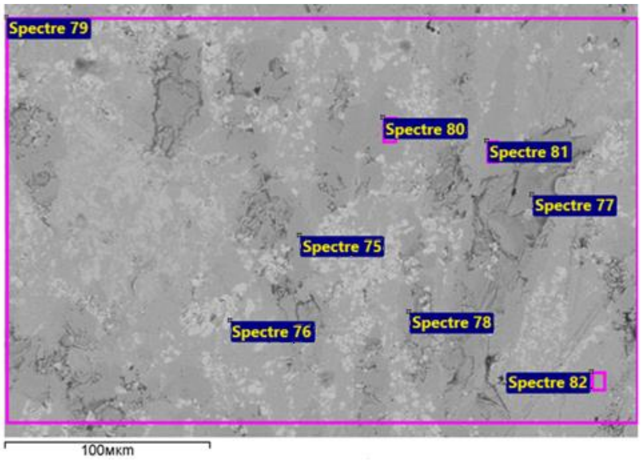


Fig. 8 Arrangement of spectra (sample No. 3)

Table 5 Micro X-ray spectral analysis (sample No. 3)

Spec-trum	75	76	77	78	79	80	81	82
C	-	0.1	0.05	-	25.1	17.5	0.07	0.08
Si	-	0.1	0.3	0.01	1.0	0.3	1.07	0.4
Cr	5.1	16.4	16.1	43.9	64.5	0.1	1.2	16.8
Mn	2.1	17.3	17.0	-	7.4	-	29.6	14.5
Fe	3.4	18.4	18.6	1.6	2.0	0.1	29.5	22.5
Co	-	17.5	19.1	1.05	-	-	1.8	14.02
Ni	-	16.2	13.5	1.3	-	3.6	23.9	18.0
Nb	45.6	8.7	7.9	6.94	-	43.1	6.7	7.4
Mo	43.8	5.4	7.45	45.2	-	35.3	6.0	6.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

However, spectra 79 and 80 confirmed the presence of a carbide phase, which was suggested in connection with the presence of carbon in the initial charge.

However, spectra 79 and 80 show a carbide phase, which is assumed, since carbon is present in the initial charge. Spectrum 81 can be interpreted as the Laves phase, which agrees with the calculated phase equilibrium diagram (**Fig. 2**).

CONCLUSION

The results of this study allow drawing the following conclusions:

1. The use of ferroalloys together with pure metals allowed obtaining alloys with high operational properties according to the HEA principle. Unlike HEAs, they did not maintain strict equiatomic concentration, so they are usually called QHEAs.
2. The addition of Mo in the amounts of 5, 10, and 15 mass% to experimental QHE alloys of the C-Fe-Cr-Ni-Co-Mn-Nb system increased hardness to 482 HV, 639 HV, and 689 HV and strength to 720 MPa, 940 MPa, and 980 MPa, respectively, while maintaining the initial plasticity.
3. Solid solutions of the FCC (Mn, Fe, Co, Ni), ICC (Nb, Mo) type, brittle and hard σ-phase (Cr, Mo), carbides Cr_3C_7, (Nb, Mo)C and Laves phases (Nb, Mo)(Fe, Ni, Mn)$_2$ were found in the structure of the studied samples.
4. The data obtained are consistent with the results of other studies devoted to the influence of Mo on the HEAs. In addition, new phases were also identified, which were suggested by the analysis of the composition of the charge materials. The formation of new phases such as carbides Cr_3C_7 and (Nb, Mo)C was observed in the studied alloys when adding ferroalloys to the charge during smelting. These new phases were not noted in other studies devoted to the effect of molybdenum on the properties of Fe-Co-Cr-Ni-Mn-Nb system alloys.
5. The innovation is that replacing pure metals with ferroalloys decreases the melting temperature, simplifying the technology for producing the alloy and positively affecting the cost of the final products.

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