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STUDYING THE STRUCTURE AND PROPERTIES OF QUASI HIGH-ENTROPY ALLOYS OF THE Fe-Co-Cr-Ni-Mn-Nb SYSTEM WITH Mo ADDITIVES

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Abstract

The paper presents the results of studying the structure, hardness and wear resistance of quasi high-entropy alloys of the Fe-Co-Cr-Ni-Mn-Nb system with Mo additives. As a result of the study, it was shown that quasi high-entropy alloys of the Fe-Cr-Mn-Ni-Co-Nb system smelted with partial use of ferroalloys and additionally alloyed with Mo in the amount of 5-15% by weight, demonstrated very system alloys without Mo additives. The structure of the studied samples is represented by a mixture of solid solutions of Mn, Fe, Co, Ni of the face-centered cubic type (FCC), Nb and Mo of the body centered cubic type (BCC), as well as interstitial phases: a carbide phase, a Laves phase and a σ-phase.

Keywords: *Quasi high-entropy alloy; Fe-Co-Cr-Ni-Mn-Nb system; Mo additives; Structure; Phases; Wear resistance*

1. Introduction

One of the present day trends in the development of alloys is developing alloys based on the “high entropy” principle. Unlike conventional alloys, high-entropy alloys (HEAs) contain at least 5 components in equiatomic concentrations, with each element having an equal chance of occupying the crystal lattice sites [1].

Thus, in HEAs, there is no the main element that forms the matrix, and the structure is represented by a solid solution of the FCC/BCC type, which includes all the elements. HEAs have excellent properties but are expensive due to the requirements for the components of the charge (only pure metals) and the complex smelting technologies.

One of the first well-studied HEA is a five-component alloy of the Co-Cr-Fe-Ni-Mn system, the so-called Cantor alloy [2]. The Cantor alloy has fairly high mechanical properties: tensile strength of 491 MPa, a yield strength of 292 MPa, while relative elongation can reach 50%, which represents a unique combination of strength and plasticity that cannot be achieved, for example, in steels or the other classical alloys.

In some papers [3-9] the effect of additional elements on the properties of the Cantor alloy is studied to improve its strength. In works [9-13] the effect of molybdenum as an additional element in the Cantor alloy is studied. It is associated with its ability to strengthen due to the large atomic radius and distortion of the crystal lattice of the alloy.

In the paper [10] the effect of molybdenum on the mechanical properties of the Fe-Cr-Co-Ni system HEAs was studied. HEAs of this system show high plasticity but at the same time have relatively low strength. It was shown that the introduction of molybdenum from 2 to 6% led to the formation of σ- and μ-phases enriched in Mo and Cr. The presence of these phases in the structure, as well as the eutectic consisting of FCC and BCC solutions, provides such a significant increase in strength.

The authors of [11, 12] noted the strengthening of high-entropy alloys with the Co-Cr-Fe-Ni-Mn base and Mo and Nb additives. The microstructural analysis of these alloys showed that with increasing the additive concentration, high-entropy matrices are formed in the structure, and new phases are released on Mo and Nb.

In [13], the authors proposed a new finely-structured high-entropy alloy CrFeNiAl0.27Si0.11Mo0.22. As a result of the experimental observations, alloys with fairly high mechanical properties were obtained: tensile strength ≥1GPa and ductility ≈15.5%.

Some works [14, 15] deal with studying the so-called quasi high-entropy alloys (QHEAs). These alloys are also developed according to the principle of “high entropy”, but they differ from HEAs in less strict observance of the requirements that are imposed on classical HEAs.

In works [16, 17], QHEAs of the Fe-Cr-Mn-Ni-

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Co-Nb system were obtained with partial use of ferroalloys in the charge. Such elements as Fe, Cr, Mn and Nb were introduced into the alloy in the form of ferroalloys. The properties of the obtained experimental alloys were comparable with the properties of similar HEAs, but their cost was significantly lower, which increases their commercial attractiveness.

It should be noted that the results considered above [10-13] relate specifically to HEAs and cannot be simply transferred to the alloys obtained by the method indicated in the papers [16-18]. This is due to the fact that ferroalloys some of which are partially used in the charge, are multicomponent systems, in particular, they contain carbon and silicon. The presence of these elements in the system certainly affects the phase formation process and so, the structure and properties of the alloy.

The purpose of this work is to study the effect of molybdenum on the structure and some properties of the Fe-Cr-Mn-Ni-Co-Nb system QHEAs smelted with partial use of ferroalloys.

2. Materials and methods

The following materials were used as charge materials: ferromanganese FeMn80C05, ferrochrome FK005, ferroniobium FNb60, nickel cathode grade H1, metallic cobalt K1Au and ferromolybdenum grade FMo60. The chemical composition of the charge components is given in Table 1. The charge composition was calculated so that the Mo content was 5, 10, 15% by weight, the Nb content was about 14% by weight, and the content of the remaining elements was approximately equal in concentration.

The dispersion of all the components was 90% represented by the fraction of 2-3 mm. The fractional composition of the materials was determined on an analytical sieving machine AS 200 control (Retsch, Germany). Then the charge mixture was thoroughly mixed within 15 minutes in a laboratory Schatz mixer M10 (POWTEQ, China) and melted in an induction furnace UIP-0.5 (Reltec, Russia) with an enhanced cooling system in the air atmosphere. Then the resulting melt was poured into alundum crucibles, cooled, remelted and poured again. Re-melting was carried out to homogenize the structure and to eliminate liquation along the body of the ingot.

After complete cooling, samples were prepared using the ingot for analysis. The chemical composition, hardness, wear resistance and structure were studied on the experimental samples. The chemical composition was determined using a Poly Spec-F spectrometer (Italy). The structure analysis was performed using a scanning electron microscope S-3400N, equipped with a NORAN X-ray energy-dispersive spectrometer from Hitachi High Technologies Corporation (Japan). Hardness was determined on a Willson 1150 device (USA); measurements were taken at least at 5 points. Tribological tests of the samples were carried out on a Tribometer installation (CSM Instruments, Switzerland) using the measuring sliding method under the following conditions: the track length was 4 mm; the applied load was 1 N; the speed was 5 cm/s; the counterbody was a ball with the diameter of 3 mm made of WC-Co (VK6); the run was 20,000 cycles (160 m); the medium was air; preliminary treatment of the samples included ultrasonic cleaning (UC) in isopropyl alcohol. The reduced wear resistance was estimated based on the parameters of the wear groove on the sample using the formula (1):

$$\varepsilon' = \frac{W}{A} \tag{1}$$

where W is the volume of wear products, mm^3; A is the friction work, N×m.

The wear groove parameters for determining the volume of wear products were determined using a WYKO NT1100 optical profilometer (Veeco Instr.Inc, USA). The results of tribological tests were automatically processed using the Instrum X Tribometer software.

3. Results and discussion

Table 2 and Figures 1 and 2 show the results of the hardness and wear resistance of the test samples. It is seen from the results that both indicators increase with increasing the molybdenum content in the sample. With the molybdenum content of 5% by weight, the hardness and wear resistance increase almost 2-fold compared to the sample without molybdenum.

Table 1. *The charge material composition*

Element, wt. %	Mn	Nb	Fe	Cr	Ni	Co	Mo	C	Si	P	S
Material											
FeMn80C05	75.1	-	25.2	-	-	-		0.1	1.85	less 0.3	less 0.03
FH001A	-	-	32.04	68.2	-	-		0.01	0.82	less 0.02	less 0.02
FN660	-	62	35.5	-	-	-		0.3	1.8	0.04	0.05
Ni H-1y	-	-	-	-	99.95			0.01	0.002	0.001	0.001
Co K1Ay	0.03	-	0.2	-	-	99.3		0.02		0.003	0.004
FMo60	-	-	38.8	-	-	-	60.2	0.08	0.8	0.05	0.01

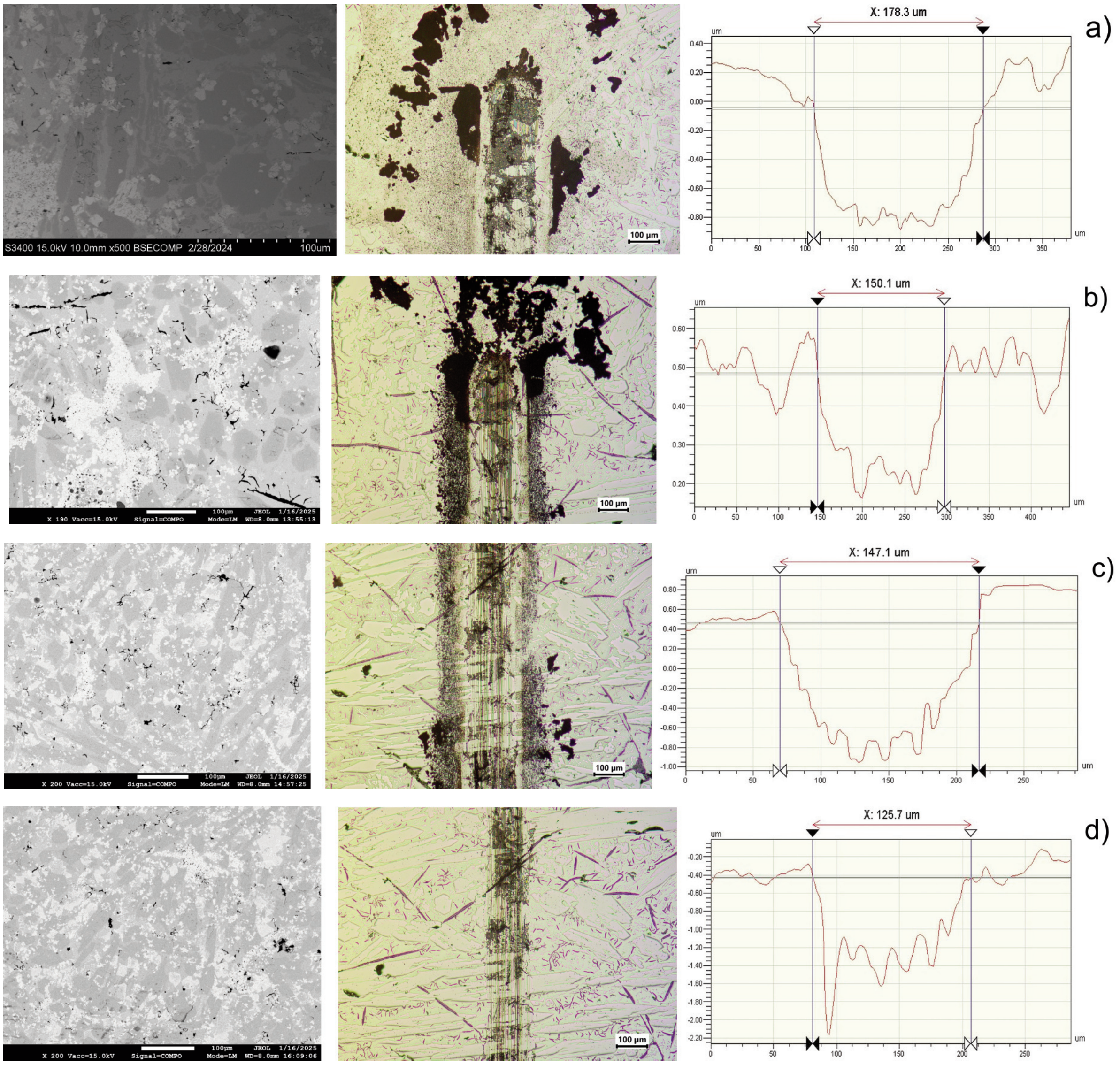


Figure 1. *Structure and wear profile of test samples: a - 0%Mo;b - 5%Mo; c - 10%Mo; d - 15%Mo*

It is also necessary to pay attention to the nature of the wear groove: if in sample No. 0 the wear profile is almost uniform, then in sample No. 3 it is intermittent. Such a difference in the nature of the profile can be explained by the structure of the studied sample: in the first case, wear occurs almost along a homogeneous surface, in the second case, the counterbody encounters solid particles on its way. The authors of the paper [10] suggested that a significant increase in hardness and strength of Fe-Cr-Mn-Ni-Co alloys additionally alloyed with Mo, is observed due to a combination of FCC + BCC solid solutions and the formation of solid Laves phases, σ- and μ-phases. However, in the studied samples, in addition to pure metals, ferroalloys were also included in the composition of the initial materials during smelting. Considering that ferroalloys are a complex system that includes such elements as C, Si, etc., it is possible to assume the formation of additional phases that will contribute to the hardness and wear resistance indicators.

For this purpose, the structures of the experimental samples were analyzed. Figure 3a shows the structure of sample No. 3. It should be noted that the nature of the structures of samples 1-3 are approximately the same: at least 4 different phases are observed (light gray, gray, dark gray and dark small interstitial phases).

The multilayer map of the distribution of elements (Figure 3b) shows an extremely uneven distribution of elements: there are clearly defined zones with the dominance of Fe, Mn, Ni and Co with the prevalence

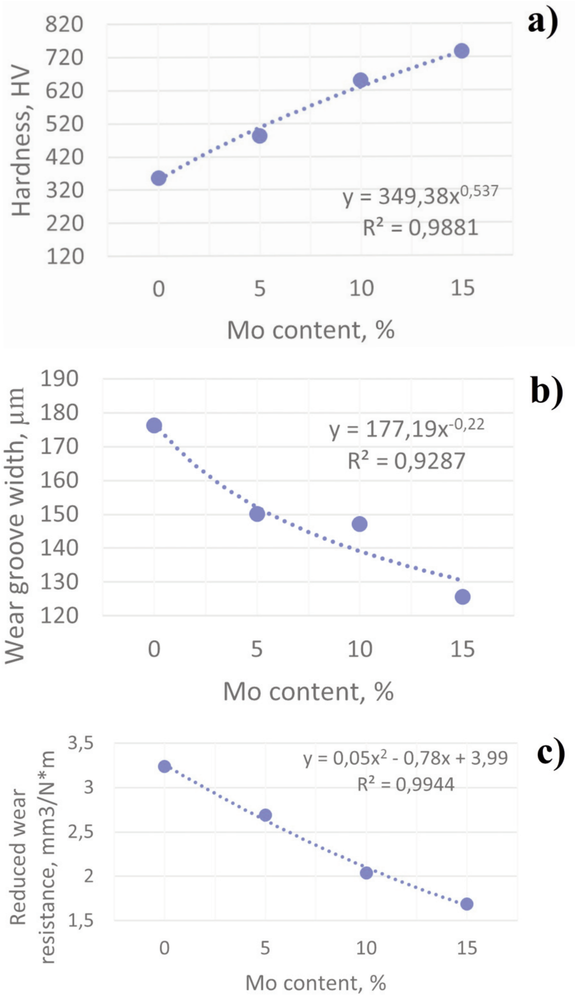


Figure 2. *The change in sample properties depending on Mo content: a – hardness, HV; b – wear groove width, µm; c – reduced wear resistance, mm³/(N×m)*

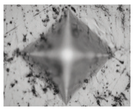
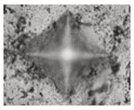
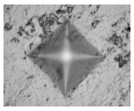
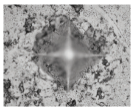
of Nb and Mo in others, etc.

To identify the phases, the micro-X-ray spectral analysis (X-ray microanalysis) was carried out (Figure 4).

To identify the above phases, the micro X-ray spectral analysis (MSA) was performed. The element distribution map shows a highly heterogeneous picture. The elements such as Mo and Nb are located in the center of the grain, while Fe and Mn are localized in the peripheral zone. To quantitatively assess the distribution of the elements, a spectral analysis was performed (Fig. 4), the results of the analysis are shown in Table 3.

It should be noted that there are traces of such elements as O, Al, P, S that can be present in the original ferroalloys. Since only traces of these elements are present (less than 10-3 %), their participation in the phase formation was not taken into

Table 2. *Hardness and reduced wear resistance of test samples*

Sample No.	Content Mo,%	quadruple pyramid impression	HV	Reduced wear resistance, mm³/(N×m)
0	0		356	3.24
1	5		482	2.69
2	10		650	2.04
3	15		736	1.69

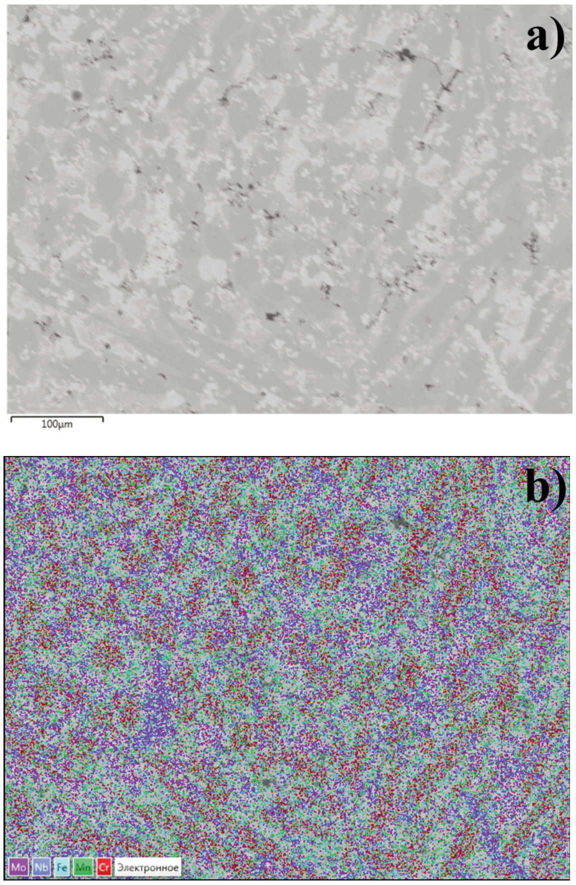


Figure 3. *Structure of sample No. 3: a – structure in the BSE mode; b – multilayer map of element distribution*

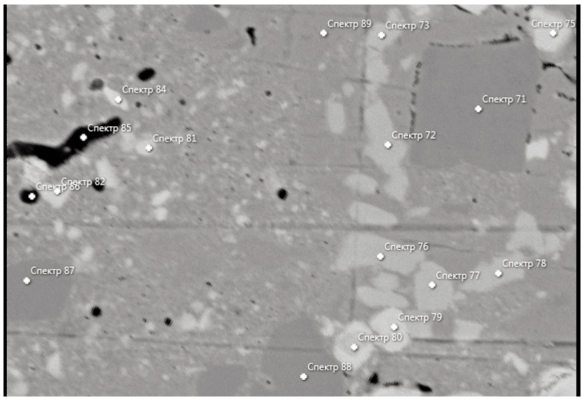


Figure 4. *Arrangement of spectra in the MRSA for phase identification*

Table 3. *Elemental composition of the spectra studied*

Spectrum	C	Si	Cr	Mn	Fe	Co	Ni	Nb	Mo	Other elements (O, P, S, Al)
Spectrum 71	0.3	0.8	13.3	18.5	19,6	19.1	19.6	3.9	3.2	rest
Spectrum 72	0.18	0.6	5.5	1.3	8.8	4.4	1.4	41.2	35.4	rest
Spectrum 73	0.2	0.4	4.2	1.6	8.3	4.1	1.5	37.2	41.6	rest
Spectrum 74	0.22	0.2	1.8	1.6	5.9	2.2	0.9	26.1	60.8	rest
Spectrum 75	0.3	0.15	1.9	0.9	1.1	0.4	0.8	55.6	37.85	rest
Spectrum 76	0.3	0.5	5.2	1.5	2.4	1.9	1.1	32.4	53.7	rest
Spectrum 77	0.15	0.2	4.6	6	8.8	9.3	15.9	19.25	35.7	rest
Spectrum 78	0.4	0.53	4.5	6	8.4	9.4	15.9	34.36	37.1	rest
Spectrum 79	0.35	0.3	2.5	0.5	3.6	6	15.5	54.3	16.9	rest
Spectrum 80	4.24	1.3	60.1	0.45	4.2	1.5	7.3	2,7	18.21	rest
Spectrum 81	1.2	1.5	2.6	0.9	1.4	1	0.8	52.6	36.7	rest
Spectrum 82	-	-	-	-	4.4	-	-	47.8	46.9	rest
Spectrum 83	0.3	1.7	5.1	3.1	4.1	1.6	1.5	46.5	35.9	rest
Spectrum 84	0.62	0.56	4.4	1.7	5.3	3.6	2.3	30.02	51.5	rest
Spectrum 85	20.6	-	29.5	23.4	26.4	-	7.8	-	-	rest
Spectrum 86	18.6	-	0.3	-	-	-	-	42.3	39.1	rest
Spectrum 87	0.2	0.34	29.9	21.9	23.3	21.9	1.3	-	-	rest
Spectrum 88	0.1	0.25	22.7	20.7	19.7	18.1	17.9	0.2	0.3	rest
Spectrum 89	0.5	1	7.6	22.8	29.6	26.5	27.6	-	-	

account.

Figure 5 shows a histogram of the distribution of elements constructed using the data in Table 3.

It can be seen from Figure 5 that the distribution of the elements in the spectra is extremely uneven: in some spectra, elements such as Nb and Mo are absent but Fe, Cr, Ni, Mn, Co are present in almost equal quantities.

The presence of C in almost all the spectra is reduced to “traces”, the exception being spectra 85 and 86.

In some spectra, Nb and Mo are present in very large quantities, about 50-60%.

The analyzed spectra can be divided into the following groups by elemental composition:

- spectra 71,87-89 are characterized by a fairly high content of such elements as Mn, Fe, Co, Ni (from 18 to 29%) and the Cr content of 13 to 20%;
- spectra 72-81 (except Spectrum 80) are characterized by a high content of Nb and Mo (from 30% and higher);
- spectrum 80 is characterized by a high content of Cr (60%) and Mo (20%);
- spectrum 82 has approximately equal amounts of Nb and Mo;
- spectrum 85 has a very high carbon content and approximately equal (about 20%) amounts of Mn, Fe, Cr;
- spectrum 86 is also characterized by a high content of carbon, Nb and Mo.

Based on the elemental composition of the spectra, the tendency of the elements to carbide formation and the type of crystal lattice, the studied phases were identified as follows:

- a solid solution of Mn, Fe, Co, Ni of the FCC type;
- a solid solution of Nb and Mo of the BCC type;
- a σ -phase (spectrum 80)
- a Laves phase (spectrum 82)
- a carbide phase of the (Cr, Fe, Mn)3C7 type (spectrum 85)
- a carbide phase of the (Nb, Mo)C type (spectrum 86)

This identification is in good agreement with the results of [10-12], with the exception of carbide

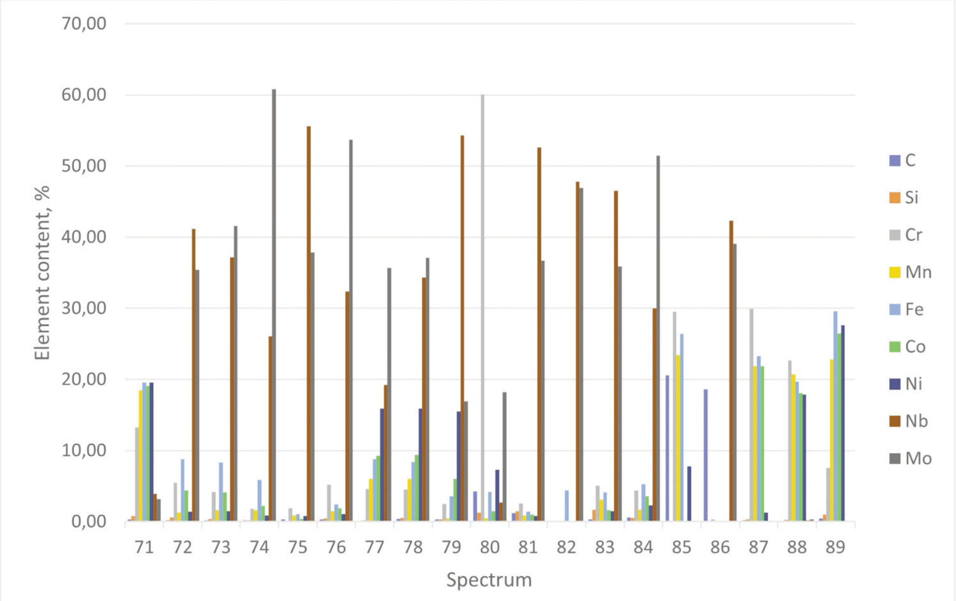


Figure 5. *A histogram of the distribution of elements constructed using the data in Table 3*

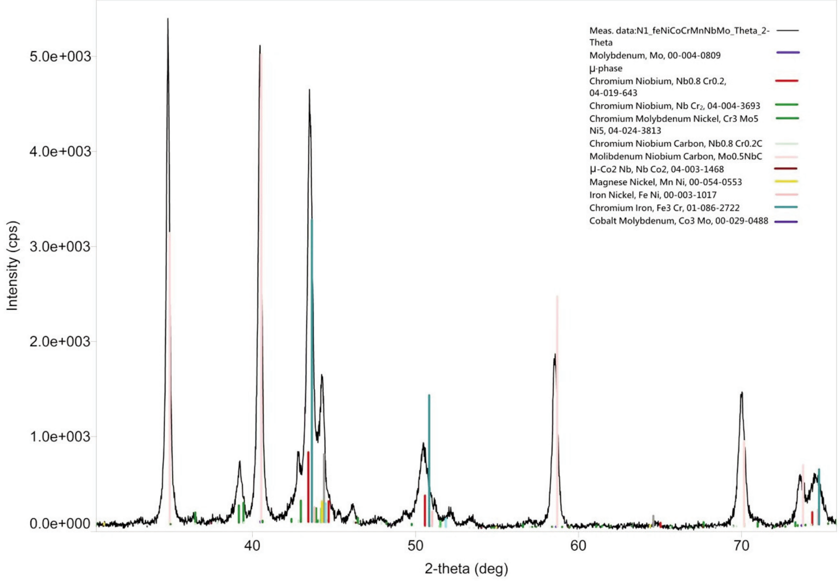


Figure 6. *Diffraction pattern of sample 3*

phases. To confirm the nature of the supposed phases, X-ray phase analysis was performed. Figure 6 shows the results of the X-ray phase analysis of sample 3. The results of the conducted X-ray diffraction confirmed the presence of the expected phases: FCC type and BCC type solid solutions; carbide phases of complex composition; Laves phases and as the presence of a μ-phase with a high Mo content.The presence of carbides in the structure is easily explained by the composition of the initial charge used in this study. In this work, ferroalloys containing carbon were partially used as components of the charge. The carbide phase also affects significantly hardness and wear resistance and apparently plays the same strengthening role as the σ-phase noted in [10].

4. Conclusion

The conducted study shows that the Fe-Cr-Mn-Ni-Co-Nb system QHEAs smelted with partial use of ferroalloys and additionally alloyed with Mo in the amount of 5-15% by weight, demonstrate very high hardness (about 730 HV) and wear resistance, which is almost 2 times higher than the hardness and wear resistance of alloys of this system without Mo additives. The structure of the studied samples is represented by a mixture of solid solutions of Mn, Fe, Co, Ni of the FCC type, Nb and Mo of the BCC type, as well as interstitial phases: a carbide phase, a Laves phase and a σ-phase.

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Author contributions

Sv.S. Kvon, V.Yu. Kulikov: Conceptualization, Methodology, Writing, Original Draft. A.Z. Issagulov, S.K. Arinova: Investigation, Writing, Formal analysis. A.R. Abildina: visualization.

Data availability

All data generated or analyzed during this work are included in this published article.

Conflicts of interests

The authors declare no conflict of interest.

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PROUČAVANJE STRUKTURE I SVOJSTAVA KVAZI VISOKOENTROPIJSKIH LEGURA SISTEMA Fe-Co-Cr-Ni-Mn-Nb SA DODATKOM Mo

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Apstrakt

U radu su predstavljeni rezultati proučavanja strukture, tvrdoće i otpornosti na habanje kvazi visokoentropijskih legura sistema Fe-Co-Cr-Ni-Mn-Nb sa dodatkom Mo. Kao rezultat istraživanja pokazano je da kvazi visokoentropijske legure sistema Fe-Cr-Mn-Ni-Co-Nb, dobijene delimičnom upotrebom ferolegura i dodatno legirane Mo u količini od 5–15% mase, pokazuju značajno bolja svojstva u odnosu na legure istog sistema bez dodatka Mo. Struktura ispitivanih uzoraka predstavljena je mešavinom čvrstih rastvora Mn, Fe, Co, Ni tipa površinski centrirane kubne rešetke (FCC), Nb i Mo tipa zapreminski centrirane kubne rešetke (BCC), kao i intersticijskih faza: karbidne faze, Lavesove faze i σ-faze.

Ključne reči: *Kvazi visokoentropijska legura; Sistem Fe-Co-Cr-Ni-Mn-Nb; Dodaci Mo; Struktura, faze; Otpornost na habanje*