

ISSN 1609-1825 (PRINT)

ISSN 2710-3382 (ONLINE)



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2 (99)
2025

2000 жылдан бастап шығарылады
Мерзімділігі жылына 4 рет

Издается с 2000 года
Периодичность 4 раза в год

Журнал Қазақстан Республикасы Ақпарат және қоғамдық даму министрлігінің жанындағы Ақпарат комитетінде тіркелген (қайта есепке алу куәлігі № KZ63VPY00044097 15.12.2021 ж.)

Журнал зарегистрирован в Комитете информации при Министерстве информации и общественно-го развития Республики Казахстан (свидетельство о перерегистрации № KZ63VPY00044097 от 15.12.2021 г.)

МЕНШІК ИЕСІ

«Әбілқас Сағынов атындағы Қарағанды техникалық университеті» коммерциялық емес акционерлік қоғамы (Қарағанды қаласы)

СОБСТВЕННИК

Некоммерческое акционерное общество «Карагандинский технический университет имени Абылқаса Сагинова» (г. Караганда)

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Information Analysis of The Molybdenum and Silicon Effect on The Properties of The Co-Cr-Fe-Ni-Mn System

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Abstract. *The paper presents the results of the information analysis of works that deal with studying the molybdenum and silicon effect on the properties of high-entropy alloys (HEA) of the Co-Cr-Fe-Ni-Mn system. The analysis shows that introducing of molybdenum and silicon has a positive effect on the strength of alloys while maintaining or even improving ductility. According to various estimates, these indicators increase on average by 1.2-1.5 times. Such an improvement in properties occurs due to the formation of interstitial solid σ - and μ - phases and Laves phases that are uniformly distributed in the viscous matrix of the solid solution in the structure. At the same time, the analysis shows that there are no works that deal with studying of technological properties, for example, fluidity. Considering the prospects for the development of quasi high-entropy alloys (QHEA) that represent a slightly different from HEA system, it seems promising to study the molybdenum and silicon effect on the properties of QHEA, since a simple transfer of the available results is not correct.*

Keywords: *high- and quasi high-entropy alloys, multicomponent matrix, molybdenum, silicon, microstructure, interstitial phases, strength, plasticity.*

Introduction. In present day industry, it is common to use traditional alloys based on one main element, while the required physical, mechanical, and operational properties are achieved by alloying with additional components.

In the early 2000s, new approaches were provided to develop multicomponent alloys that consist of five or more elements in the concentration of 5-35 atomic percent, which form a more or less homogeneous microstructure in the form of a solid solution. Such alloys are called high-entropy alloys or using the English abbreviation HEAs [1, 2].

A distinctive feature of HEAs is the formation of a single-phase thermodynamically stable solid substitution solution with a face-centered cubic (FCC) or body-centered cubic (BCC) lattice [1, 3], which determines special properties of HEAs. The unique properties of

the HEA are conditioned by the manifestation of four main effects, the so-called "HEA cocktail" [4]:

- a high value of the entropy of mixing, which increases the thermodynamic stability of the system at high temperatures and increases its resistance to the formation of undesirable phases;
- structural distortion of the crystal lattice, preventing the movement of dislocations, which in turn ensures high strength properties;
- a low rate of interatomic diffusion, which inhibits the formation of phases in the alloy;
- the effect of mixing, providing high complex characteristics.

One of the first well-studied high-strength alloys is the 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 491 MPa, yield

strength 292 MPa, while the relative elongation is up to 70%, which is a unique combination [2, 6] of strength and ductility. It cannot be achieved, for example, in steels or the other classic alloys.

At the same time, a fairly large number of works deal with improving the mechanical properties of this high-strength alloy, in particular, strength, since the existing indicator is insufficient for developing high-strength structures or products. A number of works [2-9] examine the effect of various elements on the strength and hardness of alloys of the Co-Cr-Fe-Ni-Mn system, with Ti, Nb, Mo, B, Si, etc. considered as an additional sixth element in the Cantor alloy.

The purpose of this work is an information analysis of studying the silicon and molybdenum effect on the properties of high-energy alloys of the Co-Cr-Fe-Ni-Mn system. The choice of these elements (Si and Mo) is due to the fact that they are capable of both being part of a solid solution and forming various solid interstitial phases with each of the elements included in the Cantor alloy.

Most researchers note the positive effect of introducing these elements on the strength properties of the Cantor alloy, but there are large discrepancies about the amount of the alloying element and the phase transformations in the alloy that occur as a result of its introduction.

The effect of silicon. Silicon is a relatively

inexpensive strengthening element for improving the performance properties of alloys, since it forms hard silicide phases such as Cr₃Si, Mn₅Si₃, which significantly strengthen the alloy. In addition, silicon significantly improves the fluidity of the alloy, which is of particular importance for casting alloys. However, it should be noted that there are very few studies that deal with the effect of silicon on the properties of high-alloy alloys [6-9].

Work [8] is one of the few works that studied in detail the properties of alloys obtained on the basis of the Co-Cr-Fe-Ni-Mn system with different silicon contents from 5 to 20% (series No. 2 and No. 3).

To analyze possible phase transformations caused by introducing silicon, thermodynamic analysis methods were used with the construction of ternary phase equilibrium systems and subsequent studies of the microstructure of the alloys.

It was found that the solubility of Si in the Cantor alloy reaches 7%, and in this case the structure is represented by a single-phase FCC solid solution. With increasing the silicon content to 10%, the A13 phase (symmetry class cP20) appears; in alloys with a high silicon content, the G-phase (symmetry class cF116) was found in the matrix of the A13 phase.

Figure 1 shows the phase equilibrium diagram calculated by the author of [8], which allows predicting changes in a multicomponent alloy based on the Cantor alloy.

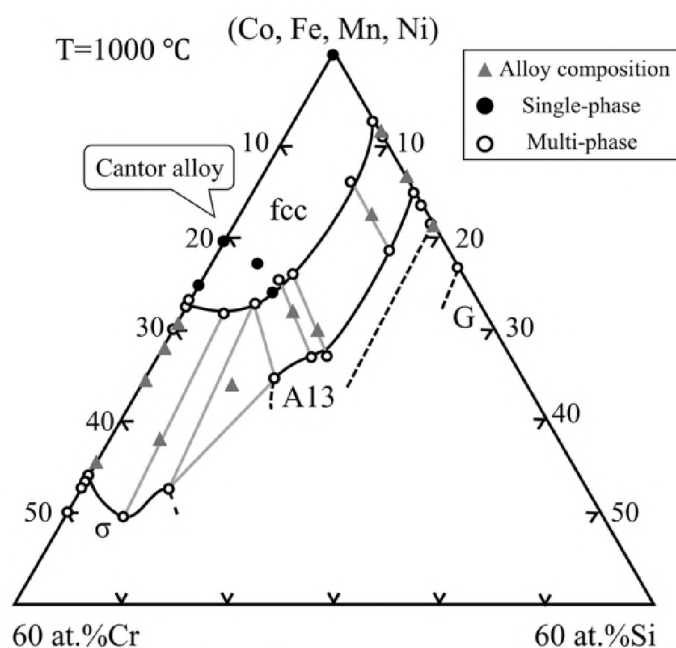


Figure 1 – Phase equilibrium diagram of alloys of the Co-Cr-Fe-Ni-Mn system with Si addition [8]

The appearance of new phases, such as the Al₃ phase and the G-phase in the alloy structure, clearly lead to changing the strength properties.

The author has shown that the introduction of silicon in the studied ranges leads to increasing strength due to the formation of twins and the inhibition of dislocations with a slight increase in plasticity compared to the same indicator of the Cantor alloy.

Based on the results obtained, the author suggests that by introducing Si as the sixth element into the Cantor alloy, it is possible to obtain an alloy with higher plasticity and strength than the original parameters.

The effect of molybdenum. The effect of molybdenum as an additional element in the Cantor alloy is studied in [9-12]. This interest is explained by the sufficiently large radius of molybdenum atoms, which leads to significant distortion of the crystal lattice of the alloy and so, to strengthening.

In addition, molybdenum has a positive effect on reducing temper brittleness, which makes it a virtually "mandatory element" in improved steels. It is logical to assume that molybdenum has the same positive effect on temper brittleness in high-alloy steels.

In [9], there was studied the effect of molybdenum on the mechanical characteristics of high-alloy steels of the Fe-Cr-Co-Ni system. High-alloy steels of this system show high plasticity but at the same time they have relatively low strength. The authors of the study showed that the introduction of molybdenum from about 2 to 6% of atoms led to the formation of intermetallics of the σ - and μ -phase type (Figure 2).

The formation of these brittle but very hard phases located in the viscous matrix of the FCC solution leads to increasing the alloy strength. The tensile strength was up to 1.2 GPa, ductility up to 19%. This work has shown the possibility of increasing the HEA strength due to the formation of brittle but hard phases in the viscous matrix, without reducing ductility of the alloy as a whole.

This phenomenon is associated with the transition from a dendritic structure with the FCC lattice to a combination of FCC+BCC+ σ -structure. The researchers came to the conclusion that in this case, significant strengthening was the result of separation of the BCC and σ -phases.

In study [10], the authors carry out an experimental assessment of the possibility of synthesizing HEAs with the (Co-Cr-Fe-Ni-Mn) base enriched with borides and silicides of Mo and Nb that are formed during the thermite combustion of SHS systems. Microstructural analysis of the Co-Cr-Fe-Ni-Mn alloy with the

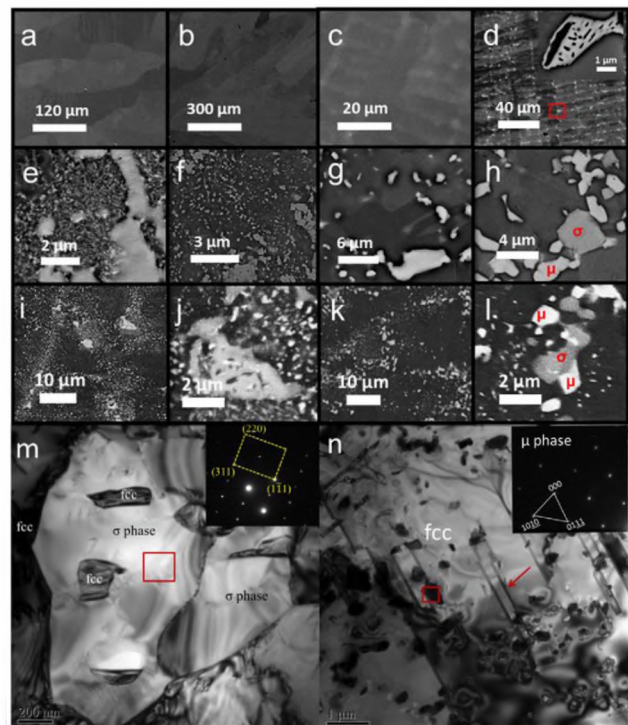


Figure 2 – SEM images of alloys with different Mo contents demonstrating the formation of σ - and μ -phases [9]

complex Mo(Nb)-Si-B additive showed that with increasing the additive concentration, high-entropy matrices were formed in the structure, and new phases based on borides and silicides (Mo and Nb) were released.

The effect of molybdenum and silicon. In [11], the authors proposed a new fine-structured high-alloy alloy CrFeNiAl_{0.27}Si_{0.11}Mo_{0.22} obtained by arc melting. As a result of the experimental observations, alloys with fairly high mechanical properties were obtained: tensile strength ≥ 1 GPa and plasticity $\approx 15.5\%$. This alloy also has excellent corrosion resistance in the 3.5% NaCl environment due to the formation of a thin molybdenum oxide film (Figure 3).

The authors of the work associate such a significant increase in strength characteristics with the formation of a fine dual structure formed by BCC plates and FCC solutions.

It should be noted that the data of this study are in good agreement with the results of work [9], where it was also noted that introducing Mo had a positive effect on strength while maintaining high ductility.

In study [12], the authors developed a new FeCoCrNiMoSix alloy with different Si contents in accordance with the atomic ratio Fe:Co:Cr:Ni:Mo:Si = 1:1:1:1:1:x (where x=0.5;1.0;1.5). The authors found that intro-

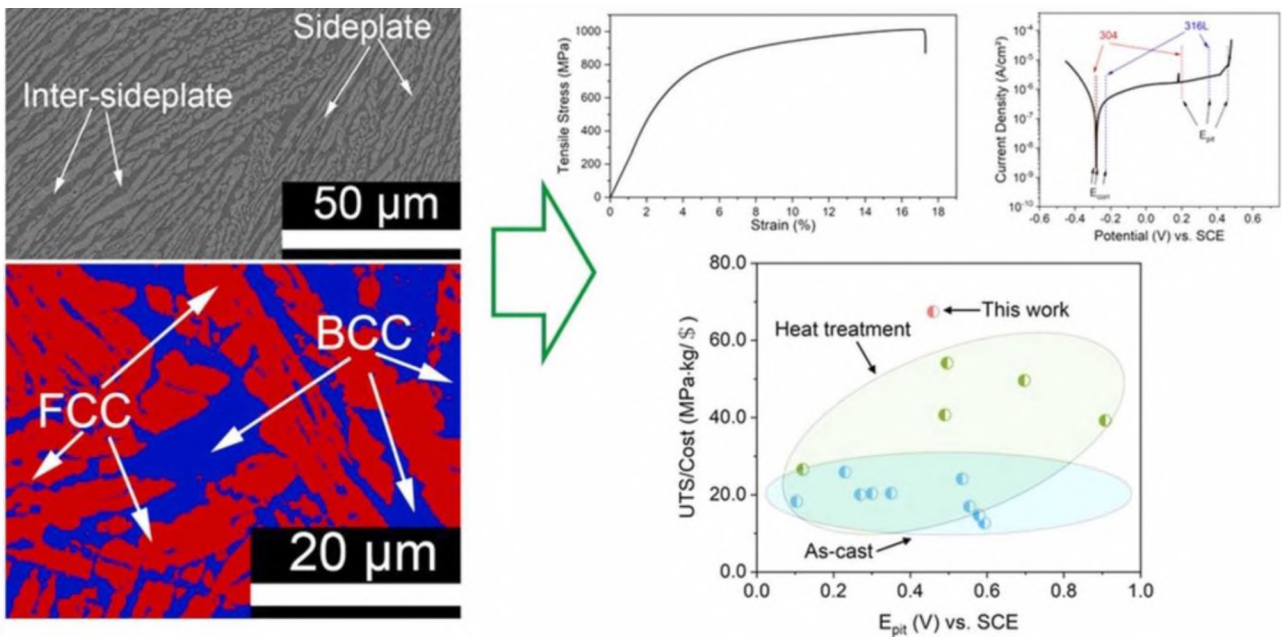


Figure 3 – Microstructure and properties of the HEA based on the CrFeNiAl_{0.27}Si_{0.11}Mo_{0.22} system [11]

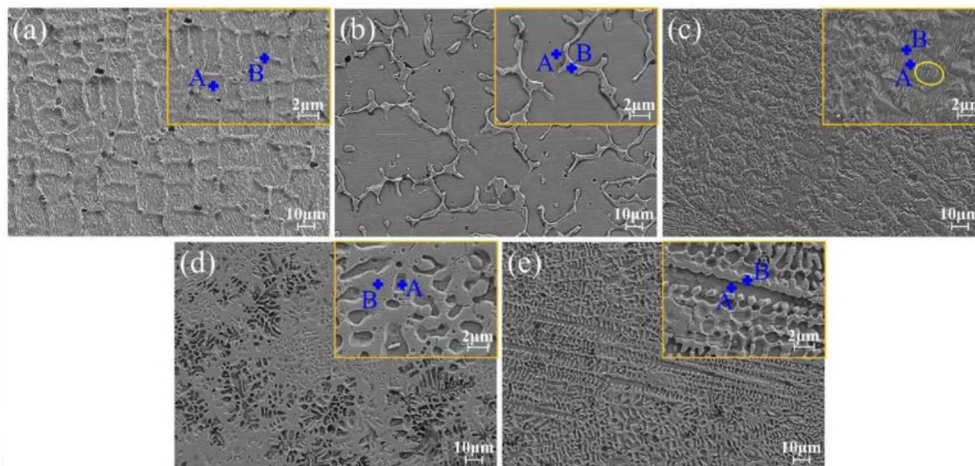


Figure 4 – Microstructure of FeCrCoMnSi_x alloys: a – x=0; b – x=0.3; c – x=0.6; g – x=0.9; d – x=1.0 [12]

ducing silicon into the FeCoCrNiMo alloy transforms the two-phase structure of the alloy into a three-phase structure of the FCC + HCP + BCC type (Figure 4). With increasing the silicon content, the structure acquires a dendritic columnar character, and with increasing the Si content to $x = 0.9$ and 1.0 , a solid silicate phase is formed in the alloy, and a clear segregation of the elements is observed.

Figure 5 shows a comparative diagram of properties constructed based on the averaged results of studies [6-12]. The HEA is under-

stood as the classical HEA of the Fe-Cr-Co-Ni-Mn system. Despite the average values of strength and plasticity, as well as some assumptions, a clear trend of the silicon and molybdenum effect on the properties of the alloy is observed. The introduction of silicon/molybdenum has a positive effect on both strength and plastic properties of HEAs. In other words, the introduction of molybdenum/silicon allows increasing the alloy strength while maintaining or even increasing the alloy plasticity.

Thus, the results of the studies in the

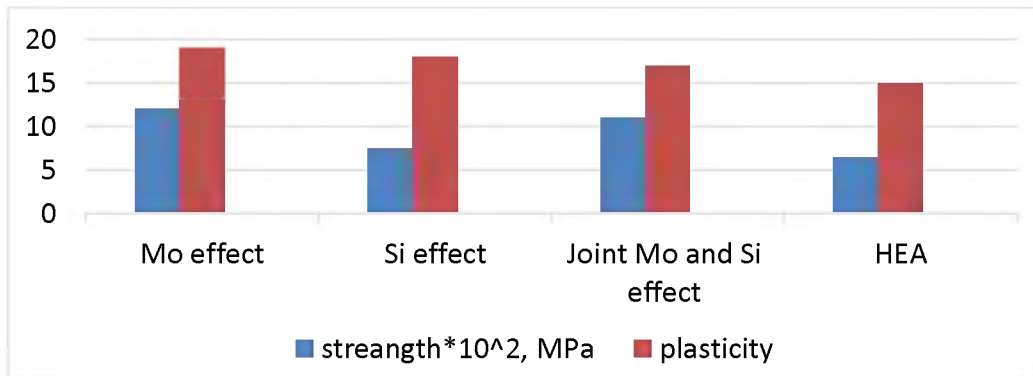


Figure 5 – Molybdenum and silicon effect on the HEA properties

above-mentioned works show that alloying of HEA with molybdenum and silicon leads to significant strengthening, and in some cases ductility of the alloys remains at the same level or even increases. It should be noted that molybdenum has a greater effect on the alloy strength than silicon. The effects of molybdenum and silicon on ductility are comparable. The combined effect of silicon and molybdenum also significantly increases the strength-ductility complex. This allows concluding that the use of molybdenum/silicon or their combined introduction as additional elements in the composition of HEAs based on the Fe-Cr-Co-Ni-Mn system allows improving the strength-ductility complex.

It should be noted that most studies focus on studying the mechanical properties of HEAs or its phase equilibrium directly. There are practically no works related to studying the casting properties of HEAs, in particular, fluidity. This is due to the fact that despite the unique properties of HEAs, they have not yet found wide practical application because of their high cost. This is due to high requirements for charge materials, since it is customary to smelt HEAs using pure metals, as well as the production technology, etc.

One of the latest trends of development of high-entropy alloys has been the development of so-called quasi high-entropy alloys (QHEAs) [13-15]. Unlike HEAs, QHEAs do not adhere to strict equiatomic concentration; simpler smelting technologies or simpler charge materials are used. In work [15], ferroalloys were partially used as charge components, which made it possible to reduce the smelting temperature, to simplify the production technology and, as a result, to reduce the cost of the alloy. It should be noted that the properties of the obtained QHEA were somewhat lower than the properties of the corresponding HEA but significantly exceeded the properties of steels

used in this segment today. Work [15] showed the prospects of research in this area. It is obvious that with partial use of ferroalloys as a charge during smelting the QHEA, the other phase transformations occur than when using pure materials, therefore, a simple translation of the obtained results of the Mo and Si effect to the new system is impossible. In addition, it is necessary to study the effect of these elements on the other properties of alloys, in particular, the casting ones, since due to the lower cost, QHEAs have a greater chance of being introduced into production.

Conclusions. The carried out information analysis showed a positive effect of Mo and Si on the strength and ductility of Fe-Cr-Co-Ni-Mn alloys. Strengthening of alloys while maintaining or even increasing ductility occurs due to the formation of new interstitial σ - and μ -phases and Laves phases that are uniformly distributed in the viscous matrix of the solid solution. All the studies concern only "classical" HEAs, therefore the obtained results cannot be simply translated into QHEAs, since they represent completely different initial phase systems. The other properties of HEAs, for example fluidity that is an important technological characteristic, were also not studied. Accordingly, studying the Mo and Si effect on strength, ductility and the other properties is a relevant and promising task.

The work was carried out within the framework of implementing the IRN Program BR21882240 "Developing a quasi high-entropy alloy using Kazakhstan raw materials and technology of producing precision parts based on it" (agreement with the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan No. 378-PTsF-23-25 dated November 15, 2023), funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan.

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Молибден мен кремнийдің Co-Cr-Fe-Ni-Mn жүйесінің ЖЭҚ қасиеттеріне әсерін ақпараттық талдау

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Аңдатпа. Жұмыста молибден мен кремнийдің Co-Cr-Fe-Ni-Mn жүйесінің жоғары энтропиялық қорытпаларының (ЖЭҚ) қасиеттеріне әсерін зерттеуге арналған жұмыстарды ақпараттық талдау нәтижелері келтірілген. Талдау көрсеткендей, молибден мен кремнийді енгізу иілгіштікті сақтай отырып немесе тіпті жақсарта отырып, қорытпалардың беріктігіне оң әсер етеді. Бұл көрсеткіштер әр түрлі бағалаулар бойынша орта есеппен 1,2-1,5 есе артады. Бұл қасиеттердің жақсаруы қатты ерітіндінің тұтқыр матрицасында біркелкі бөлінген σ - және μ - фазалары мен Лавес фазалары типін енгізудің қатты фазаларының құрылымында пайда болу арқылы жүреді. Сонымен қатар, талдау көрсеткендей, технологиялық қасиеттерді, мысалы, сұйық сұйықтықты зерттеуге арналған жұмыстар жоқ. ЖЭС-тен сәл өзгеше жүйені білдіретін квази-жоғары энтропиялық қорытпалардың (КЖЭҚ) даму перспективасын ескере отырып, молибден мен кремнийдің КЖЭҚ қасиеттеріне әсерін зерттеуге арналған зерттеулер жүргізу перспективалы болып көрінеді, өйткені қолда бар нәтижелердің қарапайым трансферті дұрыс емес.

Кілт сөздер: жоғары және квази-жоғары энтропиялық қорытпалар, көп компонентті матрица, молибден, кремний, микроқұрылым, енгізу фазалары, беріктік, икемділік.

Информационный анализ влияния молибдена и кремния на свойства ВЭС системы Co-Cr-Fe-Ni-Mn

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Аннотация. В работе представлены результаты информационного анализа работ, посвященных исследованию влияния молибдена и кремния на свойства высокоэнтропийных сплавов (ВЭС) системы Co-Cr-Fe-Ni-Mn. Анализ показал, что введение молибдена и кремния оказывает положительное влияние на прочность сплавов при сохранении или даже улучшении пластичности. Эти показатели по разным оценкам увеличиваются, в среднем, в 1,2-1,5 раза. Такое улучшение свойств происходит за счет образования в структуре твердых фаз внедрения типа σ - и μ - фаз и фаз Лавеса, равномерно распределенных в вязкой матрице твердого раствора. В то же время анализ показал, что нет работ, посвященных исследованию технологических свойств, например, жидкотекучести. Учитывая перспективность развития квазивысокоэнтропийных сплавов (КВЭС), которые представляют несколько иную систему, отличную от ВЭС, представляется перспективным провести исследования, посвященные изучению влияния молибдена и кремния на свойства КВЭС, т.к. простой трансфер имеющихся результатов не является корректным.

Ключевые слова: высоко- и квазивысокоэнтропийные сплавы, многокомпонентная матрица, молибден, кремний, микроструктура, фазы внедрения, прочность, пластичность.

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СОДЕРЖАНИЕ

РАЗДЕЛ 1. МАШИНОСТРОЕНИЕ. МЕТАЛЛУРГИЯ.....	3
КӘРІМ А., ИБРАЕВ С. Анализ конструктивных решений экзоскелетов для нижних конечностей	3
ДОСПАЕВ М.М., ФИГУРИНЕНЕ И.В. Анализ способов воздействия на расплав с целью обеспечения гомогенной структуры слитка.....	10
АРИНОВА С.К., АЛТЫНОВА А.Е. Состав шлаков металлургических заводов Карагандинской области: научный обзор.....	16
RATUSHNAYA T., DROBYSHEV A., SHAKIROVA M. The Necessity of Post-Processing Products Manufactured Using Additive Technologies.....	21
KVON S., ABILDINA A., OKISHEV K., KULIKOV V. Information Analysis of The Molybdenum and Silicon Effect on The Properties of The Co-Cr-Fe-Ni-Mn System	27
ЛУ Н.Ю., АХМЕТОВ А.С., МАХАМБЕТОВ Е.Н., КАБЫЛКАНОВ С.К., ONURALP Yü. Перспективы производства феррохрома с нулевым углеродным следом в Казахстане	35
ШЕРОВ К.Т., КУАНОВ И.С., САГИТОВ А.А., ИМАНБАЕВ Е.Б., БОБЕЕВ А.Б. Исследование шероховатости обработанной поверхности при термофрикционном фрезеровании с импульсным охлаждением стали HARDOX 450.....	41
ТАУРБАЕВ А.Е., КЫЗЫРОВ К.Б., МИТУСОВ А.А. Гидравлические ударные механизмы: анализ конструкций и применение	48
РАЗДЕЛ 2. ГЕОТЕХНОЛОГИИ. БЕЗОПАСНОСТЬ ЖИЗНЕДЕЯТЕЛЬНОСТИ	55
ЧЖАО В., АЛИШЕВА Ж.Н., БАЙБОТАЕВА С.Е. Анализ эффективности применения волновых технологий в нефтедобыче	55
SATTAROVA G., SPATAYEV N., NELYUBINA E., BALABAS L., DEMINA T. Assessing the Professional Risk of Electricians Who Service Substations at The Karagandy Zharyk LLP.....	61
РАГДАНОВА А.А., МАТАЙБАЕВА И.Е., ЗИМАНОВСКАЯ Н.А., АЙТБАЕВА С.С., ДОЛГОПОЛОВА А. Геологическое строение, минеральный состав и перспективная оценка Сугатовского месторождения	68
ЖАНАКОВА Р.К., АЛМЕНОВ Т.М., САРЫБАЕВ М.А. Исследование напряженно-деформированного состояния горных пород вокруг транспортного штрека на примере Акбакайского рудного поля.....	74
НУРПЕИСОВА М.Б., РЫСБЕКОВ К.Б., КАСЫМКАНОВА Х.-К.М., КЫРГЫЗБАЕВА Г.М., РАХИМОВ Г. Инновационные методы мониторинга деформационных процессов при освоении Жиландинских групп месторождений.....	80

УНИВЕРСИТЕТ ЕҢБЕКТЕРІ • ТРУДЫ УНИВЕРСИТЕТА 2025. №2. 478 с.

№ KZ63VPY00044097 қайта есепке алу куәлігі 2021 жылдың 15 желтоқсанында Қазақстан Республикасы Ақпарат және қоғамдық даму министрлігінің жанындағы Ақпарат комитетімен берілген (алғашқы тіркеу куәлігінің № 1351-Ж 04 шілде 2000 жыл)

Свидетельство о перерегистрации № KZ63VPY00044097 от 15 декабря 2021 года выдано Комитетом информации при Министерстве информации и общественного развития Республики Казахстан (первоначальное регистрационное свидетельство № 1351-Ж от 04 июля 2000 года)

Редакторлар – Редакторы

Р.С. Искакова, К.К. Сагадиева

Компьютерлік ажарлау және беттеу – Компьютерный дизайн и верстка

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Халықаралық индекстеу жөніндегі маман – Специалист по международной индексации

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Жарыққа шыққан күні	19.06.2025	Дата выхода в свет
Пішімі	60×84/8	Формат
Көлемі, б.т.	59,8	Объем, п.л.
Таралымы	300	Тираж
Тапсырыс	61	Заказ
Индексі	74379	Индекс

Электронный сайт журнала: <http://tu.kstu.kz/>

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Отпечатано в типографии НАО «Карагандинский технический университет имени Абылқаса Сагинова». Адрес типографии и редакции: 100027, г. Караганда, пр. Н. Назарбаева, 60.