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Using the Method of Probabilistic Deterministic Experiment to Assess the Impact of Alloying Elements on the Properties of the Quasi High-Entropy Alloy of the Fe-Cr-Ni-Co-Mn System

Abildina A.R.^{1*}, Issagulov A.Z.¹, Shcherbakova Ye.P.², Kvon Sv.S.¹

¹Abylkas Saginov Karaganda Technical University, Karaganda, Kazakhstan

²Kaliningrad State Technical University, Kaliningrad, Russia

*corresponding author

Abstract. This article considers the issues of planning experiments in testing wear resistance, hardness and tensile strength of the Cantor alloy. Basic experiments were carried out and an experimental matrix was developed. An experimental planning matrix was developed and calculated to conduct the basic experiments. The input and output parameters of the experiment were determined. The following were selected as input parameters: the niobium content from 14 to 18%; the carbon content from 1.5 to 2.5%; press pressure from 80 to 100 MPa. The output parameters were wear resistance, hardness and tensile strength. As a result, a six-factor matrix of experiments on five levels was used, in which three factors were vacant. Based on the data obtained, experiments were carried out on smelting an experimental quasi high-entropy alloy of the CoCrFeMnNi system with different niobium contents under laboratory conditions.

Keywords: experiment planning, wear resistance, hardness, press pressure, alloying elements, Cantor alloy, factors, correlation, high-entropy alloy.

Introduction

High-entropy alloys (HEA) are a current trend in improving structural metallic materials [1]. Currently, there is a significant number of studies focused on the development of high-entropy alloys based on various technologies [2-6]. Study [4] presents a traditional composition of the CoCrFeMnNi system material (Cantor alloy) that demonstrates the potential for using such materials for subsequent experiments. The study reveals that the CoCrFeMnNi system forms a homogeneous solid solution with a face-centered cubic lattice. Study [5] demonstrates that the addition of such alloying elements as Ti, Nb, V and B provides improved mechanical properties, which makes this HEA suitable for real use. The main disadvantage of all high-entropy alloys is their high price compared to traditional materials. This is due to both the composition of the charge, since high-entropy alloys are produced using pure metals, and the characteristics of the technological process, which includes mandatory remelting, accelerated crystal formation and the other methods aimed at increasing the structure homogeneity. In recent years, the development of so-called quasi high-entropy alloys (QHEA), for which the requirements to the structure are less stringent, has become popular [6].

The basic principle of developing quasi high-entropy alloys is similar to that used for high-entropy alloys (HEA). In this case, a multi-component system consisting of at least five elements is used. However, in quasi high-entropy alloys, the equiatomic concentration of components is less strictly observed, and the criteria for the charge and smelting technology are much simpler. This circumstance makes quasi high-entropy alloys more commercially attractive, while their characteristics can be comparable with the parameters of high-entropy alloys.

1. Experimental part and discussion of results

To determine wear resistance, hardness and compressive strength of the Cantor alloy, the method of probabilistic deterministic experiment was used [7, 8].

To use the method of probabilistic deterministic experiment, experiments were previously conducted to select input and output parameters. The following input parameters are selected: niobium content from 14 to 18%; carbon content from 1.5 to 2.5%; pressing pressure from 80 to 100 MPa (deterministic).

The output parameters were assumed to be wear resistance, hardness, and ultimate strength (probabilistic). These studies aim to determine the dependence of the mechanical properties, in particular, the wear resistance and hardness of the casting on various factors of its manufacture – chemical composition, melting temperature, casting configuration, heat treatment, impact of pressing, etc. The simultaneous effect of all factors at a certain value gives some specific and practically reproducible result, therefore, we can talk about the existence of an objective fundamental multifactorial dependence [9-11]. However, the type of such dependence is not defined [12-13]. Therefore, the final result of the casting properties can be determined only by several, usually two or three, factors [14-15]. Therefore, the use of the method of probabilistic deterministic experiment is very relevant.

Table 1 shows the experimental factors for the content of alloying elements and press pressure and their numerical values. Table 2 shows the plan of the 6-factor experiment at 5 levels.

The decomposition process was modeled using the method of six-factor probabilistically deterministic experimental planning. So, with 6 factors (k) influencing the process, varying at 5 levels (n), the following number of calculations and experiments (N) have to be performed: $N = pC = 56 = 15,625$. For this reason, the mathematical

planning method is used in both numerical and physical modeling of the process under study, which makes it possible to reduce the number of experiments by tens and hundreds of times.

Table 1. Experimental factors for the content of alloying elements and press pressure

Factors		Factor levels				
		1	2	3	4	5
X_1	Nb content, %	14	15	16	17	18
X_2	C content, %	1.5	1.7	2	2.3	2.5
X_3	Press pressure, MPa	80	85	90	95	100
X_4	Vacant factor	1	2	3	4	5
X_5	Vacant factor	1	2	3	4	5
X_6	Vacant factor	1	2	3	4	5

Table 2. Plan of the 6-factor experiment at 5 levels

X_1	X_2	X_3	X_4	X_5	X_6	Wear resistance, %	Hardness, HV	Compressive strength limit, MPa
14	1.5	80	1	1	1	88	370	630
14	2	90	3	3	3	72.6	360	630
14	1.7	85	2	2	2	78	290	650
14	2.5	100	5	5	5	72.5	300	670
14	2.3	95	4	4	4	88	360	625
16	1.5	90	2	5	4	93.2	310	680
16	2	85	5	4	1	94	360	630
16	1.7	100	4	1	3	87	360	570
16	2.5	95	1	3	2	82	390	680
16	2.3	80	3	2	5	78	370	665
15	1.5	85	4	3	5	76	360	690
15	2	100	1	2	4	86.5	370	640
15	1.7	95	3	5	1	93	330	690
15	2.5	80	2	4	3	82	300	550
15	2.3	90	5	1	2	82	340	655
15	1.5	100	3	4	2	87.1	360	660
15	2	95	2	1	5	82	360	670
15	1.7	80	5	3	4	72	330	640
15	2.5	90	4	2	1	87.3	330	660
15	2.3	85	1	5	3	81	335	635
17	1.5	95	5	2	3	75	320	630
17	2	80	4	5	2	89	330	660
17	1.7	90	1	4	5	93	430	690
17	2.5	85	3	1	4	93	390	660
17	2.3	100	2	3	1	91	370	645

The data in Table 2 were processed using the least squares method and partial dependences were obtained in the form of linear and polynomial functions of the type:

$$Y(X) = a + bX, \quad (1)$$

$$Y(X) = c_0 + c_1X^l + \dots + c_nX^m, \quad (2)$$

where a, b, c_i are fixed coefficients;

X is a variable (factor).

Partial dependences of the optimization parameter are wear resistance, hardness and compressive strength:

1) on factor X_1 (p_{niobium} , Nb content, %), equations of the form:

$$\begin{aligned}
 Y_{wear.1} &= -1.67x_1^2 + 54.362 x_1 - 354.5 \\
 Y_{hard.1} &= -4.7143x_1^2 + 155.06x_1 - 915.63 \\
 Y_{str.1} &= 3.2x_1 + 629.4
 \end{aligned}
 \tag{3}$$

2) on factor X_2 (p_{carbon} , C content, %):

$$\begin{aligned}
 Y_{wear.2} &= -2.6691 x_2^2 + 9.3383 x_2 + 76.791 \\
 Y_{hard.2} &= -52.34x_2^2 + 210.98x_2 + 143.52 \\
 Y_{str.2} &= 22.455x_2^2 - 101.44x_2 + 758.2
 \end{aligned}
 \tag{4}$$

3) in factor X_3 ($p_{pressure}$, press pressure, MPa):

$$\begin{aligned}
 Y_{wear3} &= -0.0226 x_3^2 + 4.2057 x_3 - 110.12 \\
 Y_{hard.3} &= -0.0657x_3^2 + 12.409x_3 - 232.2 \\
 Y_{проч.3} &= -0.3029x_3^2 + 54.954x_3 - 1829.4
 \end{aligned}
 \tag{5}$$

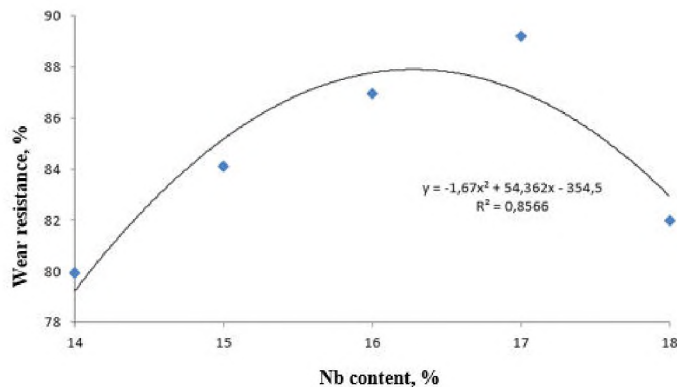
Table 3 shows the experimental values of wear resistance, hardness and compressive strength of the Cantor alloy.

Table 3. Calculated values of partial functions

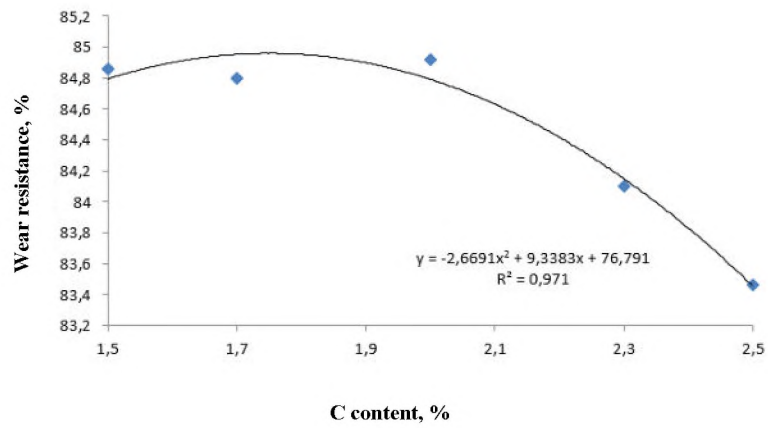
Function	Level					Average value, \bar{Y}_{av} .
	1	2	3	4	5	
Wear resistance						
$y = -1.67x_1^2 + 54.362 x_1 - 354.5$	79.82	83.9	86.84	88.2	81.88	84.128
$y = -2.6691 x_2^2 + 9.3383 x_2 + 76.791$	83.86	84.6	84.82	84	83.36	84.128
$y = -0.0226 x_3^2 + 4.2057 x_3 - 110.12$	81.8	84.4	85.62	84	84.82	84.128
Hardness						
$y = -4.7143x_1^2 + 155.06x_1 - 915.63$	336	340	358	68	343	349
$y = -52.34x_2^2 + 210.98x_2 + 143.52$	344	348	356	55	342	349
$y = -0.0657x_3^2 + 12.409x_3 - 232.2$	340	347	354	52	352	349
Compressive strength limit						
$y = 3.2x_1 + 629.4$	641	645	645	657	653	648.2
$y = 22.455x_2^2 - 101.44x_2 + 758.2$	658	648	646	645	644	648.2
$y = -0.3029x_3^2 + 54.954x_3 - 1829.4$	629	653	663	659	637	648.2

It is seen from Table 3 that the average values for each function coincide with the overall average value, which is the evidence of the absence of an error.

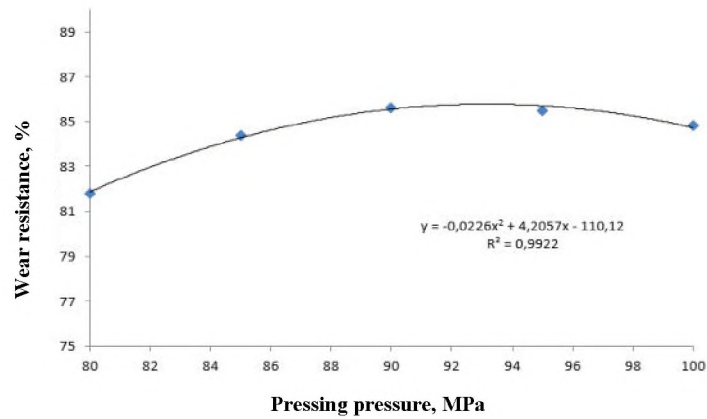
Figure 1 shows the graphs of the obtained partial dependences, constructed according to the data in Table 3.



a)



b)

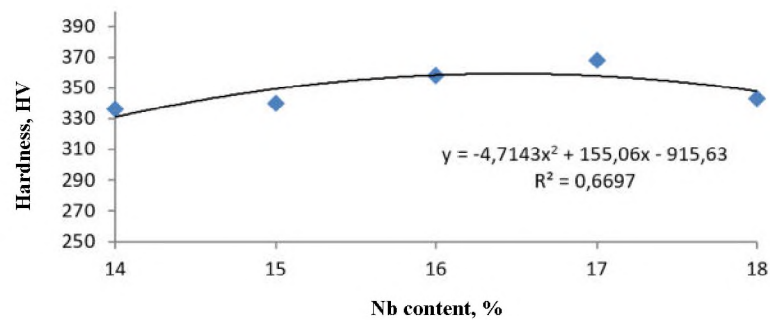


c)

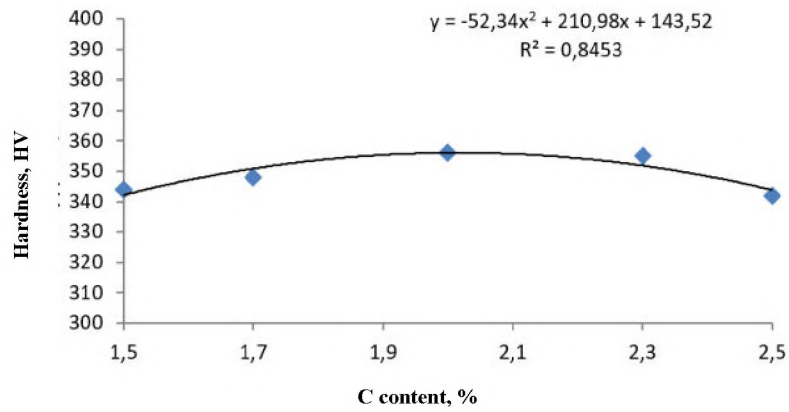
Fig.1. – Partial dependences of wear resistance of Cantor alloy: a) on the niobium content, b) on the carbon content, c) on press pressure

The correlation coefficient for each equation was $R < 1$. The correlation coefficient for comparison with experimental data for the first equation was $R = 0.8566$, for the second equation $R = 0.971$ and for the third equation $R=0.9922$. These values indicate the influence of the factor on the result.

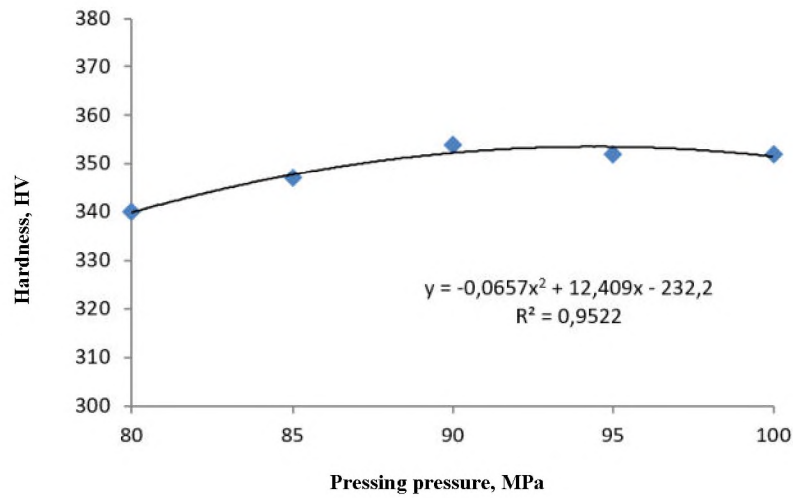
Figure 2 shows the partial dependences of the hardness of the Cantor alloy.



a)



b)



c)

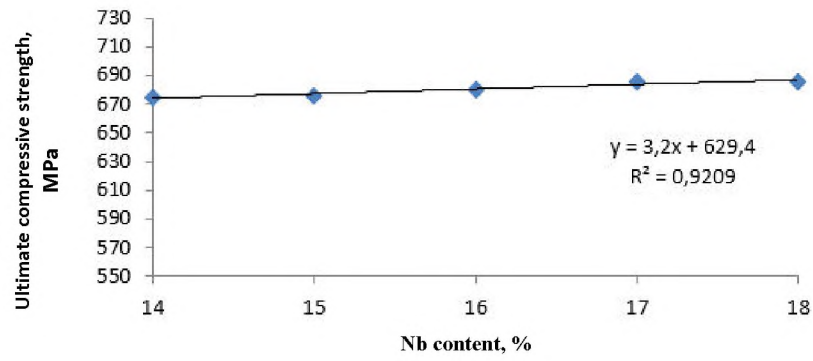
Fig. 2. – Partial dependences of the Cantor alloy hardness: a) on the niobium content, b) on the carbon content, c) on press pressure

The correlation coefficient for each equation was $R < 1$. The value of the correlation coefficient is selected automatically in Excel when constructing curves, calculated using formulas (6):

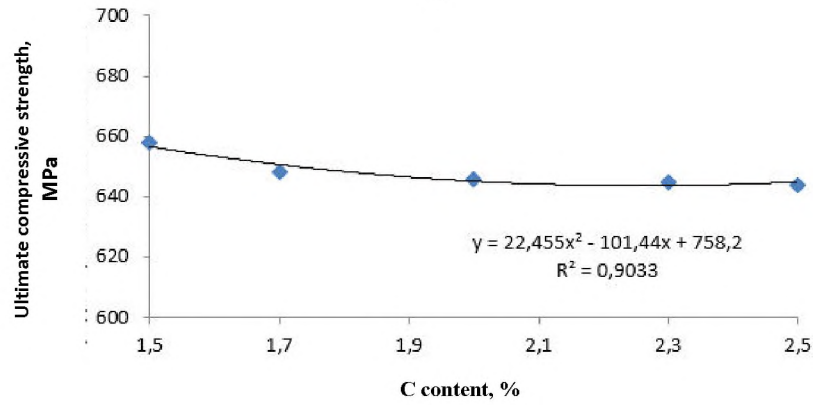
$$a_0 = \frac{\sum_{u=1}^N \bar{y}_u}{N} \qquad a_i = \frac{\sum_{u=1}^N X_{ui} \cdot \bar{y}_u}{N} \qquad (6)$$

The correlation coefficient for comparison with experimental data for the first equation was $R=0.6697$, for the second equation $R=0.8453$ and for the third equation $R=0.9522$. These values indicate the influence of the factor on the result.

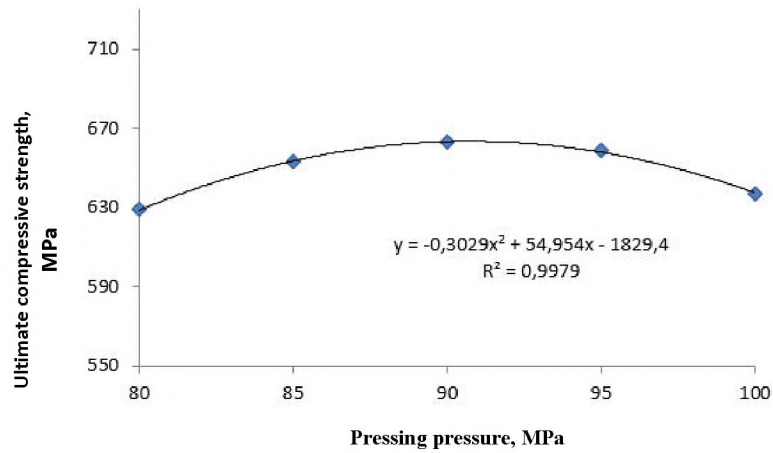
Figure 3 shows the partial dependences of the compressive strength of the Cantor alloy.



a)



b)



c)

a) on the niobium content, b) on the carbon content, c) on press pressure

Fig. 3. – Partial dependences of the compressive strength of Cantor alloy

The correlation coefficient for each equation was $R < 1$.

The correlation coefficient for comparison with the experimental data for the first equation was $R = 0.9209$, for the second equation $R = 0.9033$ and for the third equation $R = 0.9979$. These values indicate the influence of the factor on the result.

Since the average values of the calculated values of the functions completely coincided with the experimental data, the selection of private dependencies was carried out correctly.

$$\begin{aligned}
 Y_{n(\text{wear})} &= \frac{(-1.67x_1^2 + 54.362x_1 - 354.5)(-2.6691x_2^2 + 9.3383x_2 + 76.791)(-0.0226x_3^2 + 4.2057x_3 - 110.12)}{84.128^{3-1}} = \\
 &= -0.000014x_1^2x_2^2x_3^2 + 0.00265x_1^2x_2^2x_3 - 0.0694x_1^2x_2^2 + 0.00047x_1x_2^2x_3^2 - \\
 &- 0.086x_1x_2^2x_3 + 2.26x_1x_2^2 - 0.003x_2^2x_3^2 + 0.56x_2^2x_3 - 14.7x_2^2 + 0.00005x_1^2x_2x_3^2 -
 \end{aligned}$$

$$-0.009x_1^2x_2x_3+0.24x_1^2x_2+0.0016x_1x_2x_3^2+0.3x_1x_2x_3-7.9x_1x_2+0.01x_2x_3^2-1.97x_2x_3+51.5x_2+0.0004x_1^2x_3^2-0.076x_1^2x_3+1.99x_1^2-0.013x_1x_3^2+2.48x_1x_3-64.95x_1+0.09x_3^2-16.18x_3+361.7$$

$$Y_{n(hard.)} = \frac{(-4.7143x_1^2 + 155.06x_1 - 915.63)(-52.34x_2^2 + 210.98x_2 + 143.52)(-0.0657x_3^2 + 12.409x_3 - 232.2)}{349^{3-1}} =$$

$$= -0.00013x_1^2x_2^2x_3^2 + 0.03x_1^2x_2^2x_3 - 0.47x_1^2x_2^2 + 0.0005x_1^2x_2x_3^2 - 0.1x_1^2x_2x_3 + 1.9x_1^2x_2 + 0.00036x_1^2x_3^2 - 0.069x_1^2x_3 + 1.29x_1^2 + 0.004x_1x_2^2x_3^2 - 0.8x_1x_2^2x_3 + 15.5x_1x_2^2 - 0.018x_1x_2x_3^2 + 3.3x_1x_2x_3 + 62.4x_1x_2 - 0.012x_1x_3^2 + 2.27x_1x_3 - 42.4x_1 - 0.026x_2^2x_3^2 + 4.88x_2^2x_3 - 91.36x_2^2 + 0.1x_2x_3^2 - 19.68x_2x_3 + 368.3x_2 + 0.07x_3^2 - 13.4x_3 + 250.5$$

$$Y_{str.} = \frac{(3.2x_1 + 629.4)(22.455x_2^2 - 101.44x_2 + 758.2)(-0.3029x_3^2 + 54.954x_3 - 1829.4)}{648.2^{3-1}} =$$

$$= -0.00005x_1x_2^2x_3^2 + 0.009x_1x_2^2x_3 - 0.3x_1x_2^2 + 0.0002x_1x_2x_3^2 - 0.04x_1x_2x_3 + 1.4x_1x_2 - 0.0017x_1x_3^2 + 0.3x_1x_3 - 10.56x_1 - 0.01x_2^2x_3^2 + 1.85x_2^2x_3 - 61.5x_2^2 + 0.04x_2x_3^2 - 8.35x_2x_3 + 278x_2 - 0.34x_3^2 + 62.4x_3 + 2077.8$$

(7)

After transformation there is obtained:

$$L = -0.000014C_{Nb}^2C_c^2p_{np}^2 + 0.00265C_{Nb}^2C_c^2p_{np} - 0.0694C_{Nb}C_c^2 + 0.00047C_{Nb}C_c^2p_{np}^2 - 0.086C_{Nb}C_c^2p_{np} + 2.26C_{Nb}C_c^2 - 0.003C_c^2p_{np}^2 + 0.56C_c^2p_{np} - 4.7C_c^2 + 0.00005C_{Nb}^2C_c p_{np}^2 - 0.009C_{Nb}^2C_c p_{np} + 0.24C_{Nb}^2C_0 + 0.0016C_{Nb}C_c p_{np}^2 + 0.3C_{Nb}C_c p_{np} - 7.9C_{Nb}C_c + 0.01C_c p_{np}^2 - 1.97C_c x_3 + 51.5C_c + 0.0004C_{Nb}^2 p_{np}^2 - 0.076C_{Nb}^2 p_{np} + 1.99C_{Nb}^2 - 0.013C_{Nb} p_{np}^2 + 2.48C_{Nb} p_{np} - 64.95C_{Nb} + 0.09p_{np}^2 - 16.18p_{np} + 361.7$$

$$HV = -0.00013C_{Nb}^2C_c^2p_{np}^2 + 0.03C_{Nb}^2C_c^2p_{np} - 0.47C_{Nb}^2C_c^2 + 0.0005C_{Nb}^2C_c p_{np}^2 - 0.1C_{Nb}^2C_c p_{np} + 1.9C_{Nb}^2C_c + 0.00036C_{Nb}^2 p_{np}^2 - 0.069C_{Nb}^2 p_{np} + 1.29C_{Nb}^2 + 0.004C_{Nb}C_c^2 p_{np}^2 - 0.8C_{Nb}C_c^2 x_3 + 15.5C_{Nb}C_c^2 - 0.018C_{Nb}C_c p_{np}^2 + 3.3C_{Nb}C_c p_{np} + 62.4C_{Nb}C_c - 0.012C_{Nb} p_{np}^2 + 2.27C_{Nb} p_{np} - 42.4C_{Nb} - 0.026C_c^2 p_{np}^2 + 4.88C_c^2 p_{np} - 91.36C_c^2 + 0.1C_c p_{np}^2 - 19.68C_c p_{np} + 368.3C_c + 0.07p_{np}^2 - 13.4p_{np} + 250.5$$

$$R = -0.00005C_{Nb}C_c^2 p_{np}^2 + 0.009C_{Nb}C_c^2 p_{np} - 0.3C_{Nb}x_2^2 + 0.0002C_{Nb}C_c p_{np}^2 - 0.04C_{Nb}C_c p_{np} + 1.4C_{Nb}C_c - 0.0017C_{Nb} p_{np}^2 + 0.3C_{Nb} p_{np} - 10.56C_{Nb} - 0.01C_c^2 p_{np}^2 + 1.85C_c^2 p_{np} - 61.5C_c^2 + 0.04C_c p_{np}^2 - 8.35C_c p_{np} + 278C_c - 0.34p_{np}^2 + 62.4p_{np} + 2077.8$$

The obtained dependence was compared with some experimental values of the wear resistance and hardness of the samples. The samples shown in Table 4 were compared.

Table 4. Conditions for obtaining samples

Sample	Nb content, %	C content, %	Pressing pressure, MPa
1	14	1,5	80
2	15	2	100
3	16	2,5	95
4	17	1,5	95

Table 5. Comparison of research results obtained by computational and experimental methods

Sample	Wear resistance			Hardness		
	Experiment	Calculation	The discrepancy	Experiment	Calculation	The discrepancy
1	88,9	87,4	1,69	373	385	3,12
2	86,7	85,2	1,74	376	370	1,60
3	82,3	81,1	1,46	391	379	3,07
4	75,9	75,2	0,92	328	337	2,67

As can be seen from the comparative data, the discrepancy between the calculated and experimental values of wear resistance and hardness is about 1.5-3.0%.

The obtained generalized equation is adequate and can be used to determine the wear resistance (L_{NbCP}), hardness (HV_{NbCP}) and compressive strength (R_{NbCP}) of the Cantor alloy castings with the niobium content of 14-18%, the carbon content of 1.5-2.5%, and press pressure of 80-100 MPa.

The increase in wear resistance, hardness and compressive strength of the Cantor alloy with increasing the niobium content occurs in the form of a polynomial curve, that is, with the niobium content of 17%, they have higher wear resistance that is equal to $\approx 89.2\%$, hardness that is equal to ≈ 368 HV and compressive strength that is equal to ≈ 657 MPa. The greatest increase in wear resistance, hardness and compressive strength occurs with the carbon content of 84.92%, 356 HV and 658 MPa, respectively.

The content of the Cantor alloy press pressure also affects wear resistance, hardness and compressive strength: maximum values of wear resistance $\approx 85.62\%$, hardness ≈ 354 HV and compressive strength ≈ 663 MPa with press pressure of 90 MPa.

Conclusions

The calculated dependence obtained was compared with the experimental values of wear resistance and hardness of the samples. The discrepancy between the calculated and experimental values of wear resistance and hardness is about 1.5-3.0%. Based on this, the dependencies obtained by the method of probabilistically deterministic experiment can be considered adequate in the indicated ranges of initial factors. The most rational, from the point of view of identifying the optimal level of wear resistance and hardness, is proposed: niobium content – 17%, carbon content – 2%, pressing pressure – 90 MPa. Under these conditions, maximum values of wear resistance, hardness, and compressive strength are observed.

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Information of the authors

Abildina Aizhan Rymkulkyzy, Doctoral student, Abylkas Saginov Karaganda Technical University
e-mail: aizhan--1984@mail.ru

Issagulov Aristotle Zeinullinovich, Doctor of Engineering, Professor, Abylkas Saginov Karaganda Technical University
e-mail: aristotel@kstu.kz

Shcherbakova Yelena Petrovna, PhD, Associate Professor, Kaliningrad State Technical University
e-mail: sherbakova_1984@mail.ru

Kvon Svetlana Sergeyevna, PhD, Professor, Abylkas Saginov Karaganda Technical University
e-mail: svetlana.1311@mail.ru