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## WEAR RESISTANCE AND TRIBOLOGICAL PROPERTIES OF HIGH ENTROPY COATINGS CrNiTiZrCu

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*A highly entropic alloy was first synthesized in the work by mechanical alloying followed by heat treatment in vacuum under certain conditions. The microhardness of the CrNiTiZrCu coating is not inferior and in most cases exceeds the hardness of highly entropic equiatomic alloys. The wear resistance of the CrNiTiZrCu coating is  $3 \cdot 10^{-4}$  g/min, which also meets the special steels for wear resistance. High entropy coating has a low coefficient of friction (0.04) at the level of friction of layered crystals, which distinguishes them from high-entropy alloys (about 0.4-0.6) by an order of magnitude. They turn out to be anti-friction, which in all probability leads to energy savings. The coating is already used in the manufacture of turbine blades made of steel 20X13 at a turbo-mechanical plant in Karaganda.*

**Keywords:** highly entropic coatings, target, equiatomic proportions, microhardness, wear resistance.

### Introduction

Just over 15 years have passed since the discovery of high-entropy alloys (2004) [1]. The first review was performed as a complete material science cycle “production - structure - properties” for a new class of vacuum-plasma coatings - nitrides of multi-element high entropy metal alloys in [2].

A current state analysis was made for the production of such coatings, their morphology, elemental and phase compositions, structure, substructure, stress state and functional properties depending on the main formation parameters: substrate temperature during deposition, magnitude of the bias potential supplied to the substrate, and the composition of the gas atmosphere. Then many articles appeared on the synthesis and study of various high-entropy alloys [3-9].

The latest review on HEAs was made in [10]. An analysis of more than 200 obtained high entropy alloys (HEA) allowed to establish the relationship between the electron concentration, phase composition, lattice parameter and the properties of solid solutions based on BCC, FCC lattice. The basic conditions for the appearance of high-entropy chemical compounds — the Laves phase,  $\sigma$ - and  $\mu$ -phases, are revealed. For the formation of a 100% high-entropy  $\sigma$ -phase, a necessary condition is that all the elements that make up the high-entropy alloys must form the  $\sigma$ -phase in two-component alloys in a different combination, and the electronic concentration of the alloy should be in the range of 6.7–7.3 electron/atom.

For the formation of a 100% high-entropy phase of Laves the following conditions are required: the total negative enthalpy of alloy mixing at the level of -7 kJ / mol and below; pairs with an atomic difference of more than 12%; the presence in the alloy of two elements with a mixing enthalpy of less than -30 kJ/mol, the average electron concentration should be in the range of 6-7 electron/atom.

It is shown that the ratio of the lattice parameters of solid-state HEA, determined in the experiment, to the lattice parameter of the most refractory metal of the HEA determine the magnitude of the elastic modulus. An analysis of the literature data showed that we synthesized the high-entropy alloys for the first time by us due to know-how. This effect is the basis of the Application for the Patent of the Republic of Kazakhstan filed in early 2020. The continuation of the results presented in this article has already been published by us in [11, 12]. We hope that this article will be an incentive for ongoing research.

## 1. Target preparation and coating

To prepare the CrNiTiZrCu target, micropowders of the corresponding metals were taken and mixed in equiatomic proportions. Then, the prepared powder mixture was placed in a grinding bowl of a planetary ball mill made of tungsten carbide and grinding bodies (balls with a diameter of 5-10 mm) also made of tungsten carbide, the mass of which was equal to 10 masses of the powder mixture, were added. After the glass was filled with Galosha gasoline, the lid was tightly closed and the planetary ball mill was turned on (rotation speed was 500 rpm, operation time 5 hours), Fig. 1a and b. The resulting homogenized composition was then dried in a vacuum and pressed with a mold into a flat disk with a diameter of 100 mm and a thickness of 5 mm. Next, the disk was placed in a vacuum thermo-furnace and sintered in it for 3 hours. Thus, the fabricated CrNiTiZrCu target (Fig. 1c) was used for further magnetron coating deposition at the NVN 6 facility.

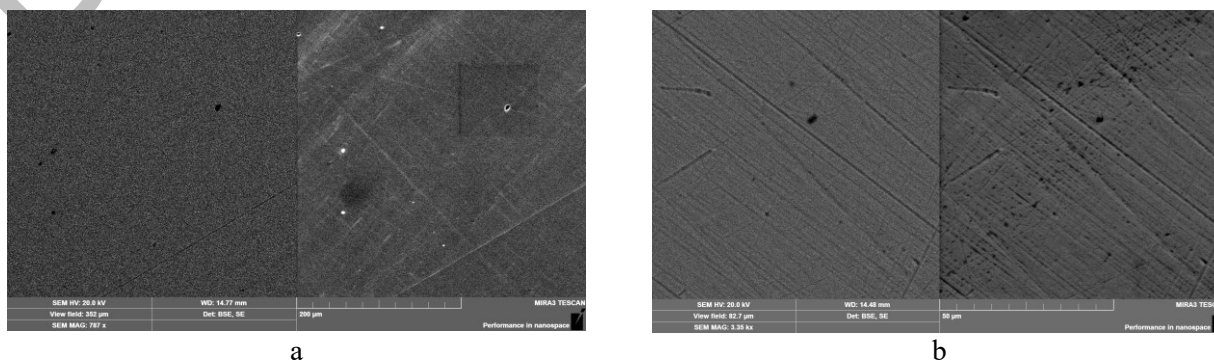


**Fig.1.** Magnetron target synthesis: a - planetary ball mill; b - micropowders of metals; c - finished target

Coating was carried out on prepared substrates made of AISI-201 steel (hexagons with a side length of 22 mm and a thickness of 5 mm.). The vacuum chamber was pumped out to a pressure of 0.003 Pa, then the PINK was turned on, and Ar was puffed up to a pressure of 1 Pa, a negative bias potential of 1000 V was applied to the substrate for 10 min. the surface of the substrate was cleaned and heated. After that, the argon pressure was lowered to 0.1 Pa and the magnetron was switched on. The bias on the substrate decreased to 150 V, the magnetron current was kept constant at 3 A. The substrate was located in the chamber at a distance of 15 cm, the spraying time was 1 hour.

## 2. Electron Microscopic Examination (EME)

Electron microscopy was carried out using a TESCAN MIRA 3 scanning electron microscope. The studies were carried out at an accelerating voltage of 20 kV and a working distance of about 15 mm. Dependencies are shown in Fig. 2.



**Fig.2.** EME of the CrNiTiZrCu coating in argon: a) 500 μm; b) 50 μm

To measure the XPS, the test sample in the form of a disk with a diameter of 8 mm and a height of 3 mm is inserted into the recess of the holder of the microscope sample (Fig. 3).

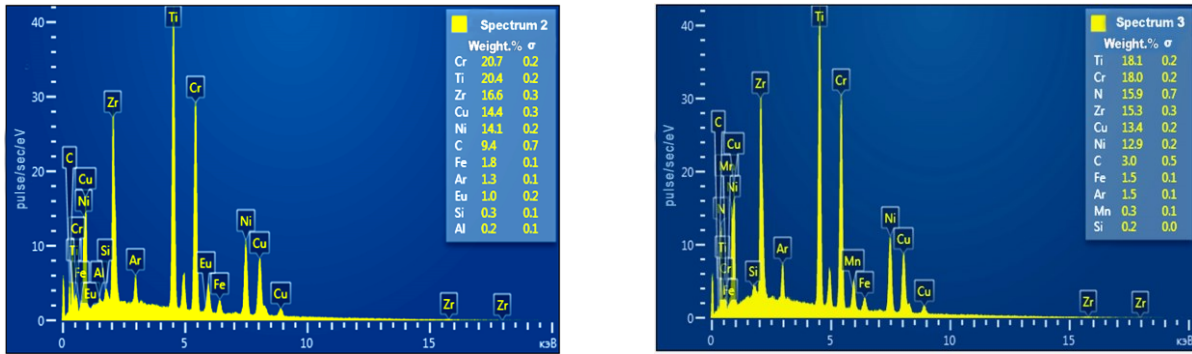


Fig.3. XPS CrNiTiZrCu in argon at 2 points

Fig.3 gives the chemical composition of CrNiTiZrCu, at.%, in equiatomic proportions (Table 1).

Table 1 - Quantitative chemical composition of CrNiTiZrCu, at. %

Element	Cr	Ni	Ti	Zr	Cu
Nominal	20	20	20	20	20
in Argon	23.2	21.2	19.9	17.1	6.8
in Nitrogen	22.8	20.8	19.7	16.9	7.0

With an increase in grinding time, the interdiffusion of the components increases and their solubility in the solid state increases until supersaturation is reached, beyond which there is no further increase in solubility (Fig. 4).

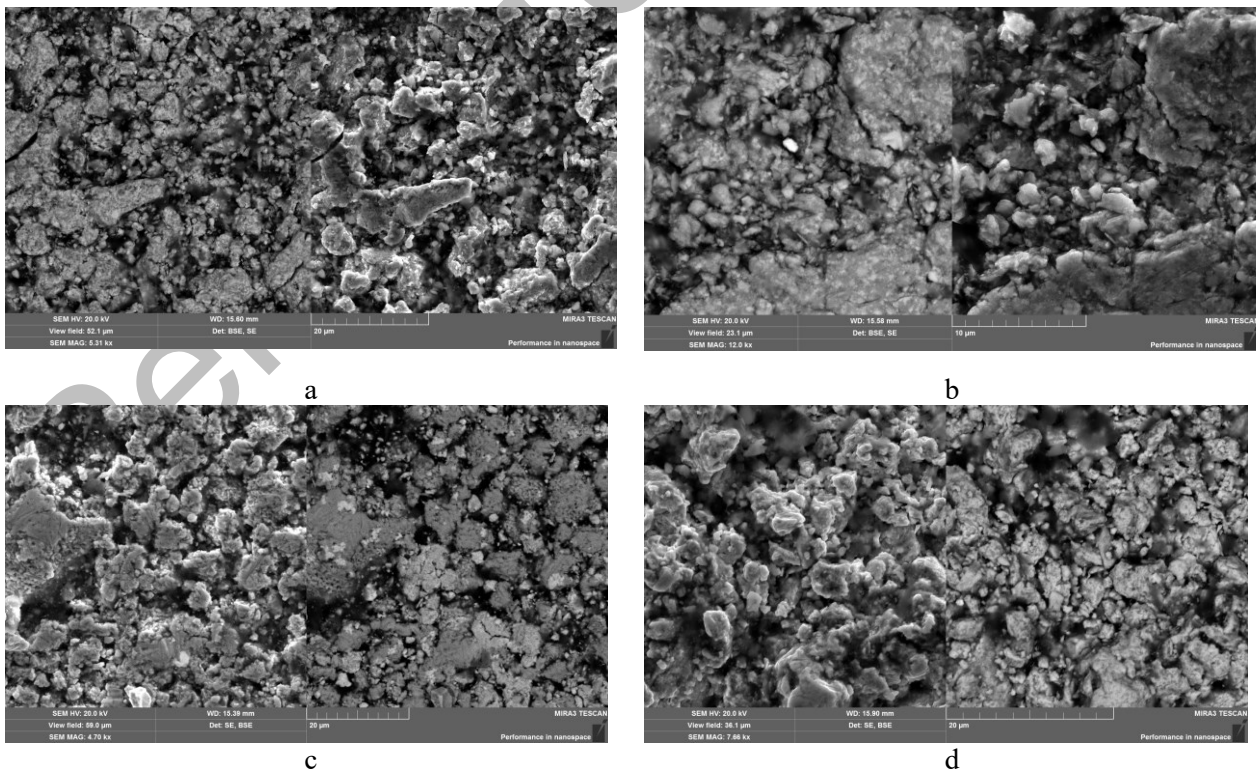


Fig.4. Microstructure of Cr-Ni-Ti-Zr components from CrNiTiZrCu alloy at a resolution: a) 20 μm; b) 10 μm; c) 20 μm; d) 20 μm.

For traditional alloys in the Cr-Ni-Ti-Zr-Cu system, the formation of many intermetallic compounds, for example, such as  $\text{Ni}_3\text{Ti}$ ,  $\text{Ni}_3\text{Cu}$ ,  $\text{Cr}_2\text{Ti}$ , is characteristic. Whereas in the obtained multicomponent CrNiTiZrCu alloy they are not formed, and it completely consists of a simple bcc solid solution, and the total number of phases is much lower than the maximum equilibrium amount allowed by the Gibbs phase rule. The predominant formation of simple solid solutions over intermetallic compounds in multicomponent equiatomic alloys is mainly provided by the influence of high entropy of mixing. According to thermodynamics, it is preferable to form phases with a low Gibbs free energy. If the enthalpy is constant, phases with a higher entropy will have lower Gibbs free energy. This effect of entropy is significantly increased for wind farms. CrNiTiZrCu alloy contains five components and its mixing entropy is  $> 1.61R$ , which is high for metal alloys, since the melting entropy of traditional alloys is  $1R$ . As a result, the Gibbs free energy of the solid solution is lower than the Gibbs energy of the intermetallic compounds; therefore, a solid solution is predominantly formed. Moreover, the melting entropy of the individual elements present in the alloy (Table 1) is lower compared to the mixing entropy of the five-component system, which is  $13.38 \text{ J/K mol}$ , which causes the formation of a simple crystalline structure of a solid solution.

### 3. Microhardness of coatings

We used the HVS-1000A microhardness tester. The results of measurements of coatings CrNiTiZrCu are given in table. 2.

**Table 2** - Microhardness of CrNiTiZrCu Coating in Argon and Nitrogen

Microhardness	1	2	3	4	5	6	7	8	The average
HV, in argon	839	909	864	842	967	753	821	902	886
HV, in nitrogen	897	899	899	863	879	887	966	962	888

The microhardness (HV) of the CrNiTiZrCu coating in the medium of argon and nitrogen did not change. This means that nitrogen does not form part of the coating. Compare the data Table 2 with the data on highly entropic alloys (Table 3).

**Table 3** - Microhardness of high-entropy alloys [2]

Alloys	Initial hardness cast alloys, HV	Alloy hardness after annealing, HV
CuTiVFeNiZr	590	600
AlTiVFeNiZr	800	790
MoTiVFeNiZr	740	760
CuTiVFeNiZrCo	630	620
AlTiVFeNiZrCo	790	800
MoTiVFeNiZrCo	790	790
CuTiVFeNiZrCoCr	680	680
AlTiVFeNiZrCoCr	780	
MoTiVFeNiZrCoCr	850	890
Stainless steel	410	362
The microhardness of our coating CrNiTiZrCu	888	888

It turned out that these cast materials, along with characteristics typical of metal alloys, had unique and unusual properties inherent, for example, to cermets: high hardness and resistance to softening at high temperatures, dispersion hardening, positive temperature hardening coefficient,

and high level of strength characteristics at elevated temperatures, attractive wear resistance, corrosion resistance and a number of other properties. It is worth paying attention to the fact that, even at high temperatures, the alloys did not lose their sufficiently high mechanical properties, which significantly exceeded the properties of traditional widely used alloys and mainly consisted of simple bcc and fcc phases. After annealing, the alloys retained high hardness, corrosion resistance, oxidation resistance, and a number of other properties. Comparative data on the values of hardness (HV) of high-entropy equiatomic and traditional alloys (using typical high-strength stainless steels and alloys of nickel, cobalt, or titanium) in the initial state and after annealing are given in table. 3. The microhardness of our CrNiTiZrCu coating is not inferior to highly entropy equiatomic alloys.

#### 4. Wear resistance of coatings

To solve these problems, an effective method of testing for microabrasive wear is applied by applying a rotating steel ball to a flat sample with the addition of an emulsion containing abrasive particles. At the point of contact, a spherical crater is formed - a calotte, therefore the device for providing this type of test was called a calotester (Fig. 5).



**Fig.5.** A device developed by us for testing materials and coatings for microabrasive wear

The results of studies of coatings are shown in table 4.

**Table 4 -** Wear resistance of CrNiTiZrCu coatings

Sample wear (weight in grams) 30 min each						
Before	15.14852	15.14857	15.14859	15.14856	The average	15.148566
After	15.14745	15.14763	15.14759	15.14759	Difference	0.000986

Tab.4 shows the wear resistance of the coating CrNiTiZrCu  $\sim 3 \cdot 10^{-4}$  g/min, which corresponds to wear-resistant coatings. The mass was measured on a torsion balance with an accuracy of 0.0001 g.

#### 5. Tribological features of CrNiTiZrCu coatings

CrNiTiZrCu was sprayed on a stationary sample for an hour with a reference voltage of 150 and 250 volts for an hour in a constant power mode of 1.5 kW. Sample No. 25 in nitrogen and sample No. 39 in argon. The friction coefficients were measured on the setup we developed [13].

**Table 5** - Friction Coefficients for Copper and Aluminum

coating	on copper		on aluminum	
	friction coefficient	error	friction coefficient	error
CrNiTiZrCu in argon	0.041	0.006	0.066	0.002
CrNiTiZrCu in nitrogen	0.057	0.001	0.077	0.004

High-entropy CrNiTiZrCu coatings turn out to be anti-friction, which in all probability leads to energy savings.

## Conclusion

Synthesis of a high-entropy alloy by mechanical alloying is more economically advantageous than remelting in a vacuum cast samples. We continue to study the CrNiTiZrCu coating on the details of machines and mechanisms, but the preliminary results look encouraging.

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