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Comparison of titanium nitride and high-entropy coatings on parts of industrial plants

V M Yurov¹, E N Eremin² and S A Guchenko¹

¹Karaganda University E.A. Buketova, st. Universitetskaya, 28, Karaganda 100028, Kazakhstan

²Omsk State Technical University, 11, Mira ave., Omsk, 644050, Russia

Abstract. The task of the work is to establish a relationship between the main parameters of high-entropy CuZrTiNiCr coatings and their mechanical properties on parts of industrial enterprises with classic titanium nitride coatings. The technique is based on the use of mechanical alloying methods for the synthesis of high-entropy alloys and the production of magnetron targets from them. The application of titanium nitride coatings and high-entropy CuZrTiNiCr coatings on the parts was carried out on an NNV-6.6I1 installation.

Establishment that high-entropy CuZrTiNiCr coatings have a density of 5.72 g/cm³, and the density of titanium nitride coatings is 5.44. The microhardness of high-entropy coatings is 14.1 GPa, while for titanium nitride coatings it varies over a wide range 20.2 GPa. The friction coefficient of titanium nitride coatings changes 0.4-0.5, which is 10 times higher than that of the high-entropy CuZrTiNiCr coating - 0.04. This antifriction property of the high-entropy coating on the parts of industrial enterprises leads to greater wear resistance and a longer service life, in comparison with classical titanium nitride coatings.

Titanium nitride coatings on industrial parts were found to be 10 times less effective than high-entropy CuZrTiNiCr coatings. This is due to the wear resistance of these coatings, which is due to the very low coefficient of friction and low surface energy.

Keywords: high-entropy coatings, titanium nitride, hardness, friction, wear resistance, phase composition.

1. Introduction

A feature of high-entropy alloys (HEAs) is that they have a high entropy of displacement and it affects the formation of solid solutions [1]. The first review (a little over 15 years) on HEAs was made in [2]. Were multifacetedly investigated, first of all, the mechanical properties of HEAs, then the magnetic, electrical and optical properties. Physical processes in HEAs differ from classical alloys in nonequilibrium properties: thermodynamic, kinetic, strong distortion of the crystal lattice, cocktail effect.

The last review on HEAs was made in [3]. There, over 200 HEAs were reviewed and found that, in addition to simple solid solutions, Laves phases, σ - and μ -phases appear under certain conditions. The appearance of these phases is due to a well-defined electron concentration in the alloy. And for the formation of Laves phases, the presence of a certain enthalpy of displacement is necessary.

Titanium nitride hardening coatings have been used in industry since the 60 s of the 20 th century as an increase in the wear resistance of cutting tools. The coatings are obtained by ion-plasma method in vacuum installations of the Bulat type. The microhardness of titanium nitride coatings varies over a wide range - from 14 to 28 GPa.

The quality of ion-plasma titanium nitride coatings strongly depends on the deposition process parameters (titanium cathode arc current, reaction gas pressure in the vacuum chamber, temperature of an industrial part). A change in technological parameters leads to a change in the content of the droplet



phase in the titanium nitride coating and a decrease in its microhardness, which ultimately deteriorates its quality.

A feature of high-entropy alloys is that their magnetron sputtering does not strongly depend on technological parameters.

Analysis of domestic and foreign literary sources showed that high-entropy alloy CuZrTiNiCr was synthesized by us for the first time. Comparison of coatings made of this alloy on industrial parts with classical coatings made of titanium nitride opens their perspective for their widespread use.

To this it should be added that we have developed a theoretical approach to predicting the properties of multi-element coatings noted in previous works [4, 5], which will be used in this work. In these works, the approaches currently used to create HEAs based on thermodynamic modeling and calculation of phenomenological parameters, but their applicability requires further refinement. Possible mechanisms of hardening in these alloys and methods of controlling them by changing the chemical composition also raise a question. Analysis of the results of recent years on high-entropy coatings did not reveal their application in industry.

In this work, the task is to establish a relationship between the main parameters of high-entropy CuZrTiNiCr coatings and their mechanical properties on parts of industrial enterprises with classical titanium nitride coatings.

2. Objects and methods of research

In [6], two methods of fabricating a magnetron target for obtaining high-entropy coatings are described. In method 1, the cathode was fabricated from an alloy with high entropy. The cathode itself with a certain ratio of chemical elements was obtained by arc melting using a very pure inert gas. Sputtering of this cathode resulted in uneven coating of the parts. This is its main drawback. In method 2, a cathode was manufactured, which contained the sought elements in the form of inserts. This is much simpler than method 1, but it has a significant drawback associated with the difference in the modes of sputtering of the inserts (arc current, reference voltage, type of reaction gas).

Therefore, for the manufacture of our magnetron targets, we took a slightly modified technology [7], which is based on the principle of mechanical alloying. This method gives coatings 15-20 cheaper than the methods of vacuum production of cast HEAs. In method 3 for the manufacture of the CuZrTiNiCr magnetron, micropowders of pure metals were poured into the container of a ball mill, which was made of tungsten carbide. The same balls 10 mm in diameter were placed in a mill, into which pure gasoline was added and then rotated at a speed of 500 rpm for 5 hours. The resulting powder was dried in a vacuum, then it was pressed into a disc with a diameter of 100 mm and a thickness of 5 mm. The manufactured disk was kept in a vacuum thermal furnace for 3 hours at a temperature of 1600 °C. At this temperature, crystallization of the composition occurred and a high-entropy alloy was obtained.

In method 4, we took steel 12Kh18N10T with a diameter of 100 mm and a thickness of 5 mm. Holes with a diameter of 12.5 mm were cut out on this circle, and pressed HEAs powders were inserted into them. Before inserting metal micropowders, they were prepared according to the above scheme.

Electron microscopic examination was carried out on a scanning electron microscope MIRA 3 from TESCAN.

All studies on the deposition of ion-plasma titanium nitride coatings on parts of industrial enterprises were carried out on a modernized automated installation NNV-6.6I1. This unit contains a vacuum chamber and a pumping system, a gas supply and water cooling system, and an electric power supply system. It also includes control and diagnostic systems. The working chamber is evacuated to a pressure of $5 \cdot 10^{-3}$ Pa. The supply of reactive or neutral gases in the form of nitrogen, oxygen or argon was carried out from the RRG-10 regulators and was measured using a vacuum gauge.

To obtain plasma from gas, we used a PINK source with a hot and hollow cathode, manufactured by our order at the ISE SB RAS. The PINK source works as follows. When gas enters the working chamber, a high voltage is applied to the electrodes by means of a magnetic field and the cathode is heated. Electrons are emitted from the thermal cathode to the electrode, which acts as an anode, which ignites the plasma. By changing the filament current, it is possible to change the energy of the

electrons that evaporate from the thermal cathode, from several tens to the order of hundreds of amperes. The resulting non-self-sustaining arc discharge generates a plasma in the working chamber, which contains $10^9 - 10^{11} \text{ cm}^{-3}$ electrons and effectively cleans the parts and nitriding them.

An arc evaporator with a magnetic arc discharge control was used to obtain a metal plasma. Titanium VT1-0 was chosen as the cathode. To control the conditions for applying titanium nitride coatings on industrial parts, it is necessary to control the plasma parameters: its concentration and potential; the temperature of its electrons and their floating potential. Plasma parameters control was automated by simultaneous measurements of the current and potential of the probe volt-ampere characteristic using a two-channel digital converter.

3. Results of the experiments and discussion

On model samples of steel 20Kh13, CuZrTiNiCr coatings were applied and investigated, shown in Figure 1 and the approximate chemical composition of which is indicated in Table 1.

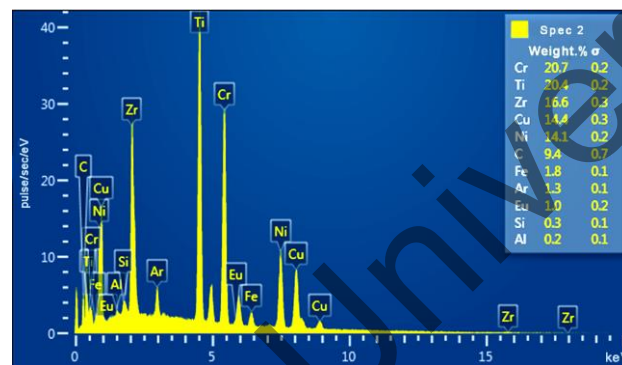


Figure 1. XPS coating CuZrTiNiCr

Table 1. Chemical composition of CuZrTiNiCr coating

Element	Cu	Zr	Ti	Ni	Cr
in argon	14.4	16.6	20.4	16.1	20.7

It is seen from the figure and the table that the magnetron target after vacuum melting acquires an equiatomic structure [8]. The phase composition and structure parameters of the deposited ion-plasma coating were studied in detail and qualitatively on an XRD-6000 X-ray diffractometer. It follows from our work [9] that out of five CuZrTiNiCr HEAs, three have an HCC structure, TiCr_2 gives rise to the Laves phase, and NiTi gives martensite with the B19' structure.

The average values of density ρ , microhardness μ , wear resistance I , and friction coefficient k for CuZrTiNiCr coatings and titanium nitride are given in Table 2.

Table 2. Properties of CuZrTiNiCr and TiN coatings

Coating	ρ , g/cm^3	μ , GPa	k	I , 10^{-4} g/min
CuZrTiNiCr	5.72	14.1	0.04	0.2
TiN	5.44	20.2	0.6	~ 3

From table 2 it follows that the wear resistance of titanium nitride is 10 times (as well as the coefficient of friction) less than that of the CuZrTiNiCr coating.

The microhardness of Cr-Ni-Ti-Zr-Cu coatings deposited in argon and nitrogen is practically the same. This means that nitrogen is not incorporated into the coating. Let's compare the data in table 2 with the data of high-entropy alloys (table 3).

Table 3. Microhardness of high-entropy alloys

Alloy	Hardness of cast alloys, GPa	Hardness of alloys after annealing, GPa
TiVFeNiZrCu	9.4	9.5
TiVFeNiZrAl	12.7	12.5
TiVFeNiZrMo	11.7	12.1
TiVFeNiZrCoCu	10.0	9.8
TiVFeNiZrCoAl	12.5	12.7
TiVFeNiZrCoMo	12.5	12.5
TiVFeNiZrCoCrCu	10.8	10.8
TiVFeNiZrCoCrAl	12.4	10.6
TiVFeNiZrCoCrMo	13.5	14.1
316 Stainless steel	3.0	2.5
17-4 PH Stainless steel	6.5	5.7
Stellite 6	6.6	7.8

The microhardness of our CuZrTiNiCr coating is not inferior to high-entropy equiatomic alloys, but significantly exceeds the microhardness of stainless steels. In [9], we showed that the CuZrTiNiCr coating consists of three fcc structures, titanium chromide (TiCr_3) corresponds to the Laves phase, and titanium nickelide (NiTi) corresponds to martensite with the B19' phase.

Let us now compare the coefficient of friction of our CuZrTiNiCr coating with the friction of high-entropy coatings investigated in [11].

The coefficient of friction of our CuZrTiNiCr coating is $k \approx 0.04$. If we take the nitride coatings of some HEAs (Table 4, below), then they have significant coefficients of friction (up to 0.96). The reason why the coefficient of friction of our coating is so small is for two reasons. First, the resulting coatings have a memory effect. Second, the resulting coatings contain a large phase of free carbon ($C = 9.4$ wt%, Fig. 1), which leads to the formation of a solid lubricant and leads to a decrease in friction.

Table 4. Coefficients of friction of high-entropy alloys

Coating	Friction coefficient, k
CuFeCoCrNiTi	0.136
WFeCoCrNiTi	0.220
ZrFeCoCrNiTi	0.240
MoFeCoCrNiTi	0.265
AlFeCoCrNiTi	0.350
(AlCrTaTiZr)N	0.760
(AlCrMoTaTiZr)N	0.800
(TiZrNbHfTa)N	0.960

The properties of titanium nitride coatings on industrial parts are mainly associated with the chemical bond of titanium and nitrogen, which is a solid homogeneous solution of the TiN_x type intercalation, where $x = 14.8\%$ to $x = 22.6\%$. This corresponds to compounds from $\text{TiN}_{0.6}$ to $\text{TiN}_{1.0}$. Such solid solutions arise when the following condition is met: $R_N/R_{\text{Ti}} < 0.59$, where R_N is the radius of the nitrogen atom and R_{Ti} is the radius of the titanium atom. The TiN coating, most often, is an fcc crystal lattice with a lattice constant $a = 0.42346$ nm. Some parameters of titanium nitride coatings are shown in Table 5.

Table 5. Titanium nitride parameters

Parameter	The quantity
Grid	Cubic face-centered B1
Lattice period, nm	0.423
Density, g/cm ³	5.213
Microhardness, GPa	20.2
Elastic modulus, Mn/m ²	25600
Melting point, °C	2950
Thermal expansion coefficient $\beta \times 10^{-6}$	9.35
Specific electrical resistance, $\mu\Omega \times \text{cm}$	25

The main disadvantage of ion-plasma sputtering of titanium nitride and the production of wear-resistant coatings from it is the formation of a droplet phase in the coating. This causes the formation of porosity in the coatings, thereby reducing the wear resistance of the parts. The droplet phase on the parts leads to an increase in their roughness, so the parts themselves need to be ground up to grade 10, which takes a lot of time. Assistance in the process of titanium nitride sputtering with the PINK system reduced the formation of the droplet phase 15 times and the coatings were of high quality.

What caused the wear of both coatings? Many researchers believe that this is primarily due to surface energy. The wear of the coating can be estimated at dry sliding friction by the formula:

$$M = A \cdot \rho \cdot k / \sigma, \quad (1)$$

where A is some constant, M is the wear mass, ρ is the coating density, k is the friction coefficient, σ is the surface energy.

All values from formula (1) are known from Table 2. The value of surface energy was determined by us according to the method described in [12] from the size dependence of microhardness. Experimentally, in the coordinates $\mu/\mu_0 - 1 \sim 1/h$ (h is the thickness of the coating), a straight line is obtained, the tangent of which gives the value of σ .

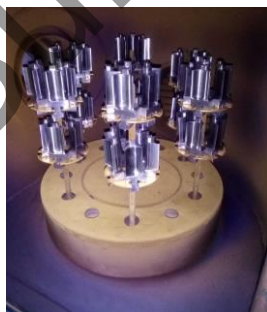
For all parts, the average values of the surface energy turned out to be equal:

$$\sigma(\text{TiN}) = 2,242 \text{ G/m}^2, \quad \sigma(\text{CuZrTiNiCr}) = 1,149 \text{ G/m}^2. \quad (2)$$

Since the densities of both coatings differ insignificantly, $M_{\text{TiN}}/M_{\text{Cu}} \approx (k/\sigma)_{\text{TiN}}/(k/\sigma)_{\text{Cu}} \approx 10$.

Further, comparative production tests of the studied coatings were carried out on turbine blades of thermal power plants; on drills; on grain crusher hammers; on flat surfaces of working bodies of agricultural machinery; on gears of mining equipment.

The general view of coated products are shown in Figure 2.

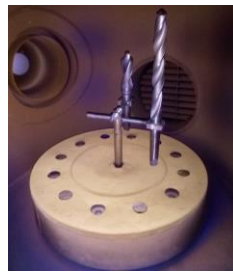


CuZrTiNiCr



TiN

a)

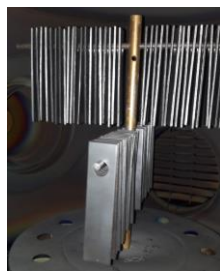


CuZrTiNiCr



TiN

b)



CuZrTiNiCr



TiN

c)



CuZrTiNiCr



TiN

d)



CuZrTiNiCr



TiN

e)

Figure 2. The general view of coated products:

a) blades for a coated turbine in a vacuum chamber NNV-6.6I1; b) coated drills in a vacuum chamber NNV-6.6I1; c) coated hammers in the vacuum chamber NNV-6.6I1; d) agricultural plowshares with coatings in a vacuum chamber NNV-6.6I1; e) coated gear

Production tests have shown that coating with CuZrTiNiCr on the parts of industrial enterprises leads to an increase in their service life by at least 4 times. We attribute such characteristics of industrial

parts with coatings to the presence in the CuZrTiNiCr coating of compounds of nickel with titanium and zirconium, which have shape memory. Such devices, after thermal effects, which arise in the process of friction of parts, can acquire their original form due to reversible martensitic transformations.

Thus, the high-entropy CuZrTiNiCr coating is 10 times more effective than the titanium nitride coating and can be successfully used for hardening coatings in industry.

4. Conclusion

Establishment that high-entropy CuZrTiNiCr coatings have a density of 5.72 g/cm³, and the density of titanium nitride coatings is 5.44. The microhardness of high-entropy coatings is 14.1 GPa, while for titanium nitride coatings it varies over a wide range 20.2 GPa. The friction coefficient of titanium nitride coatings changes 0.4-0.5, which is 10 times higher than that of the high-entropy CuZrTiNiCr coating - 0.04. This antifriction property of the high-entropy coating on the parts of industrial enterprises leads to greater wear resistance and a longer service life, in comparison with classical titanium nitride coatings.

Titanium nitride coatings on industrial parts were found to be 10 times less effective than high-entropy CuZrTiNiCr coatings. This is due to the wear resistance of these coatings, which is due to the very low coefficient of friction and low surface energy.

Shown, that two parameters of the coating, namely, the coefficient of friction and the value of surface energy determine, by and large, the efficiency and service life of parts of industrial enterprises.

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6. Acknowledgement

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