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# Microhardness and wear resistance of a high-entropy coating FeCrNiTiZrAl

V M Yurov<sup>1\*</sup>, E N Eremin<sup>2</sup> and S A Guchenko<sup>1</sup>

<sup>1</sup>Karaganda University named after E.A. Buketov, st. Universitetskaya, 28, Karaganda 100028, Kazakhstan

<sup>2</sup>Omsk State Technical University, 11 Mira Ave., Omsk, 644050, Russia

\*Corresponding author: exciton@list.ru

**Abstract.** In this article, the microhardness and wear resistance of the high-entropy FeCrNiTiZrAl alloy are studied on model specimens and on turbine blades made of 20Kh13 steel. The alloy was made by mechanical alloying and subsequent annealing in a vacuum furnace. The study showed that the obtained alloy is a high-entropy alloy with a microhardness  $\mu = 740$  HV, which is at the level of the microhardness of metallic glasses, but 2-3 times higher than the microhardness of stainless steels. The friction coefficient of the FeCrNiTiZrAl coating is  $k = 0.06$ , which is 10 times less than the friction coefficient of the titanium nitride coating ( $k = 0.65$ ). The wear resistance of the high-entropy FeCrNiTiZrAl coating is much higher than that of stainless steels, and it leads to the fact that the cost of titanium nitride coating on turbine blades is 2 times higher than the cost of FeCrNiTiZrAl coating, that is, the economic effect is obvious.

## 1. Introduction

In alloys with high entropy, when five or more equiatomic metallic elements are alloyed, solid solutions with the simplest structure are stabilized [1-3]. However, later it was shown that simple structures do not always arise, but also Laves phases and several other phases are formed [4-9]. This is especially evident in equiatomic structures obtained by mechanical alloying and magnetron sputtering of targets [10-12].

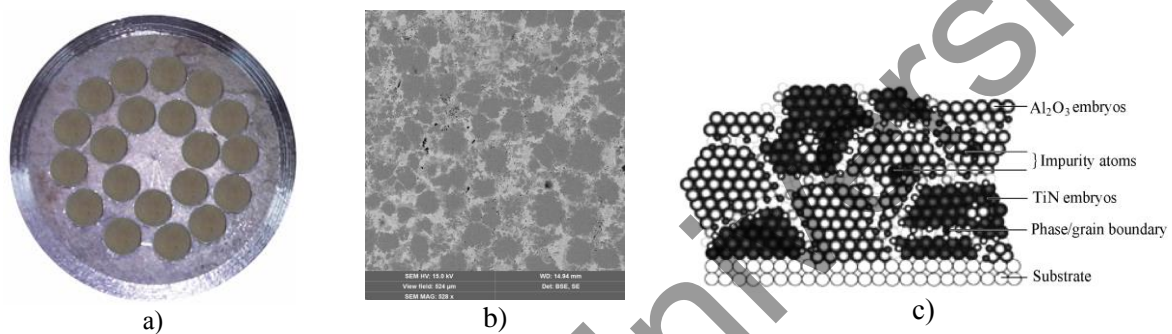
In our proposed empirical model [13], the anisotropy of the surface energy and the thickness of the surface layer of the high-entropy FeCrNiTiZrAl alloy are calculated. The thickness of the surface layer of this alloy is about 2 nm, which is an order of magnitude greater than the thickness of the surface layer of complex crystals, but is of the same order of magnitude as that of metallic glasses. The hardness and other properties of the high-entropy alloy are the same as for metallic glasses, but are 2-3 times higher than the hardness of stainless steels. The surface energy of the high-entropy FeCrNiTiZrAl alloy is about  $1.149 \text{ J/m}^2$ , which corresponds to the surface energy of magnesium oxide and other crystals with a high melting point. But unlike these crystals, the friction coefficients of a high-entropy alloy are much lower ( $\sim 0.06$ ) than that of conventional steels ( $\sim 0.8$ ). We have shown theoretically that the friction coefficient is proportionally dependent on the surface energy and inversely proportional to the Gibbs energy, which significantly decreases for a high-entropy alloy, leading to low friction.

In this article, the microhardness and wear resistance of the high-entropy FeCrNiTiZrAl alloy are studied on model specimens and on turbine blades made of 20Kh13 steel.



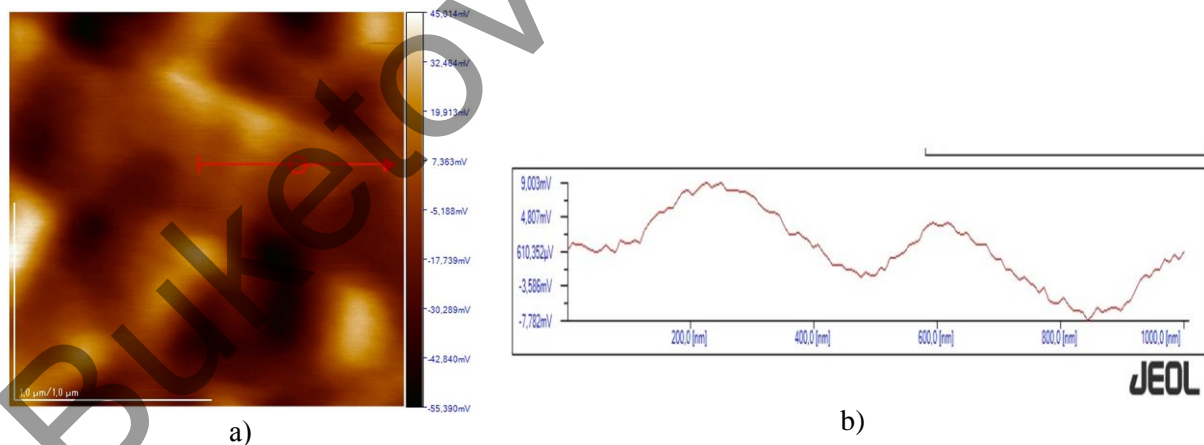
## 2. Research methods

To prepare the FeCrNiTiZrAl target, the corresponding equiatomic metal micropowders were used. Further, the obtained metal composition was loaded into a mill glass, which was made of tungsten carbide, and grinding balls with a diameter of 5-10 mm were also made of tungsten carbide. Having filled the glass of the mill with gasoline "Galosha", the mill was connected to the rotation connector at a speed of 500 gram for 5 hours. Then the metal composition was dried, pressed into a disc 100 mm in diameter and 5 mm thick, and placed in a thermal furnace in which the required vacuum was maintained. The process itself took 3 hours. The FeCrNiTiZrAl target was used for coating (Figure 1 a), nanostructured coating (Figure 1 b) and coating formation scheme (Figure 1 c).



**Figure 1.** FeCrNiTiZrAl target (a), nanostructured coating (b), coating formation scheme (c) [14]

The roughness of the FeCrNiTiZrAl coating measured with a JSPM-5400 atomic force microscope is also insignificant (Figure 2).

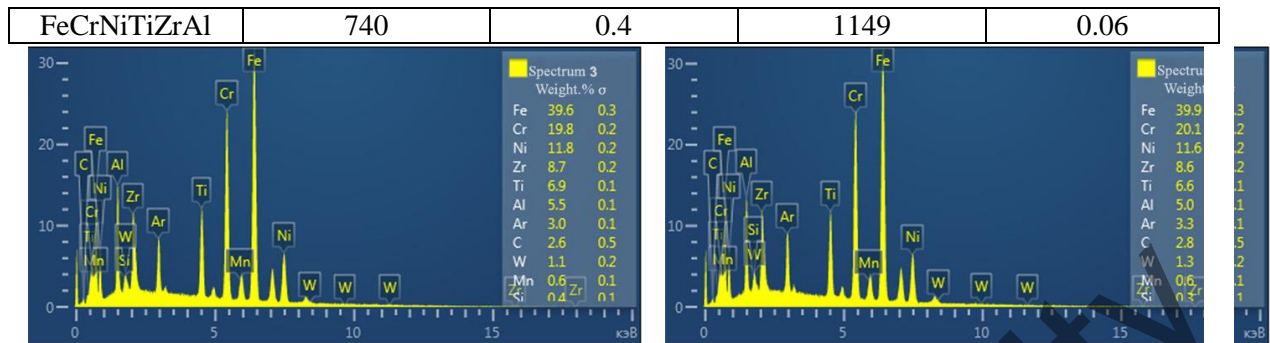


**Figure 2.** AFM image of ZrTiCrNiCu (a) and its roughness (b)

X-ray fluorescence electron spectroscopy (XPS) of FeCrNiTiZrAl coatings for argon is shown in Figure 3, and the chemical composition is presented in Table 1.

**Table 1.** Chemical composition of the target (at.%)

Alloy	Fe	Cr	Ni	Ti	Zr	Al
FeCrNiTiZrAl	39.6	19.8	11.8	6.9	8.7	5.5



**Figure 3.** XPS of FeCrNiTiZrAl coatings at two points

The chemical composition (table 1) indicates that we have a high-entropy alloy FeCrNiTiZrAl (5-40 at.%).

We used a HVS-1000A microhardness tester (Figure 4 a). The determination of the wear resistance of the coatings was carried out on a device for measuring the wear of coatings (calotest) (see Figure 4 b) by the method of decreasing mass. A steel ball (steel grade ShKh15) weighing 262 grams, 40 mm in diameter, rotated at a constant speed. Somewhat below the center of gravity of the rotating ball was the sample under study, which was touched by the rotating ball. The contact time at one point was experimentally selected 15 minutes, and the number of points was 20 (see Figure 4 b). The weight of the coatings was determined on a microbalance with an accuracy of 10 micrograms. We measured the surface energy by the method [15].



**Figure 4.** Microhardness tester HVC-1000A (a) and installation diagram for determining wear resistance (b)

### 3. Research results and their discussion

Table 2 shows the value of microhardness  $\mu$ , wear resistance  $i$ , surface energy  $\sigma$  and friction coefficient  $k$  of FeCrNiTiZrAl coatings.

**Table 2.** Mechanical properties of nanostructured coatings FeCrNiTiZrAl

Coating	$\mu$ , HV	$i$ , $10^{-4}$ g	$\sigma$ , J/m <sup>2</sup>	$k$
FeCrNiTiZrAl	740	0.4	1149	0.06

Let us now compare the mechanical properties of nanostructured FeCrNiTiZrAl coatings with the mechanical properties of stainless steels. First, we give the microhardness of stainless steels (table 3), then compare the wear resistance of steels (table 4) and finally, present the friction coefficients  $k$  (table 5).

**Table 3.** Microhardness of stainless steels [16]

Steel	$\mu$ , HV	Steel	$\mu$ , HV	Steel	$\mu$ , HV	Steel	$\mu$ , HV
316	189	Stellite 6	413	18Kh2N4MA	269	20KhGNR	197
17-4 PH	410	Hastelloy C	236	15KhCND	335	34KhN1M	229

**Table 4.** Wear resistance of steels [17]

Steel	$i$ , $10^{-4}$ g	Steel	$i$ , $10^{-4}$ g	Steel	$i$ , $10^{-4}$ g	Steel	$i$ , $10^{-4}$ g
Kh15	40	12KhN3A	50	38KhC	30	38KhN3MA	20
20Kh13	40	20Kh2N4A	20	30KhGAW	30	40Kh	70

**Table 5.** Coefficients of friction of steels on metals [18]

Alloy	Element	$k$	Alloy	Element	$k$
Steel	Graphite	0.10	Steel	Wolfram carbide	0.60
Steel	Brass	0.35	Steel	Nickel	0.64
Steel	Copper	0.53	Steel	Steel	0.80

Comparison of tables 2 with table 3 shows that the microhardness of stainless steels is almost 2 times less than the microhardness of the nanostructured FeCrNiTiZrAl coating. This means that the studied coating has a hardness much higher than stainless steels and is less susceptible to wear (that is, destruction of the coating), as evidenced by the comparison of tables 2 with table 4. The destruction of the coating is due to the appearance of a new surface [19], which is associated with its surface energy  $\sigma$ . Surface energy in the process of destruction is converted first into plastic deformation, then into elastic deformation, then into thermal motion, and finally into surface energy. The surface energy is formed due to several atomic monolayers (about 10 nm) in the surface layer, which differs from the properties of the bulk phase and is a strictly nonlinear system. In this layer, stress concentrators arise when a metal sample is loaded, which leads to the destruction of the material and coatings. The first concept of surface energy was proposed by A. Griffiths [20], taking the value of  $\sigma$  as the energy required for the destruction of a solid, while the work of destruction is equal to  $-A = \sigma S$ , where  $S$  is the surface area of the solid.

We noticed that high-entropy alloys (HEA) are similar in microhardness to metallic glasses (MG) (table 6).

**Table 6.** Mechanical properties of high-entropy alloys and metallic glasses.

HEA	$\mu$ , HV [21]	MG	$\mu$ , HV [22]
CrNiTiZrCu	890	Fe <sub>40</sub> Ni <sub>40</sub> P <sub>14</sub> B <sub>6</sub>	640
AlTiVFeNiZr	800	Fe <sub>78</sub> P <sub>13</sub> C <sub>7</sub>	760
MoTiVFeNiZr	740	Fe <sub>78</sub> Si <sub>10</sub> B <sub>12</sub>	890
CuTiVFeNiZrCo	630	Ni <sub>75</sub> Si <sub>8</sub> B <sub>17</sub>	860
MoTiVFeNiZrCo	790	Co <sub>75</sub> Si <sub>15</sub> B <sub>10</sub>	910

AlTiVFeNiZrCoCr	780	Ti <sub>50</sub> Be <sub>40</sub> Zr <sub>10</sub>	730
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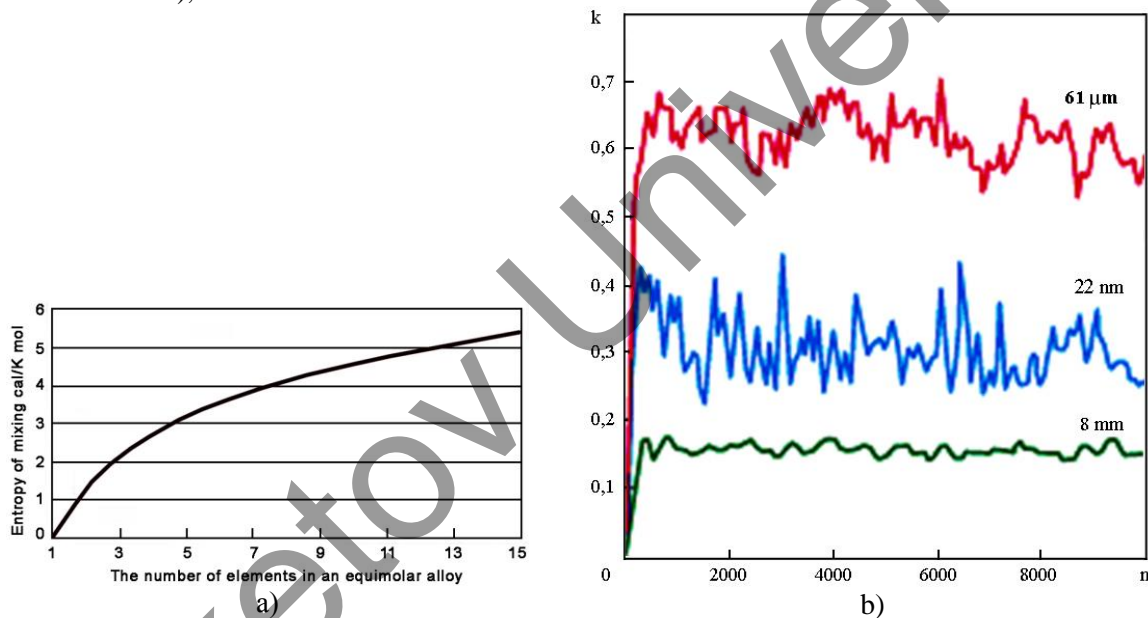
From table 6 it follows that HEAs have microhardness at the level of metal glasses, but much higher than that of stainless steels (table 3). This means that the mechanisms for the formation of HEAs are similar to those of metallic glasses.

Comparison of tables 2 with table 4 shows that the wear of the FeCrNiTiZrAl coating is 2 orders of magnitude ( $\sim 100$ ) less than the wear of stainless steels. This is due to the fact that the wear of the steel, like that of the coating, is determined not only by the state of the surface, but also by the friction between the samples. The coefficient of friction of the FeCrNiTiZrAl coating with a sample of exactly such a coating is  $k = 0.06$ , and steel-steel (Table 5) -  $k = 0.80$ , i.e. an order of magnitude less.

In [21], we theoretically obtained the formula:

$$k = \tilde{N} \cdot \dot{O} \cdot \frac{\sigma \cdot S}{\Delta G^0} \cdot \bar{N}, \quad (4)$$

where  $\sigma$  is the specific surface energy of the material,  $S$  is the contact area,  $T$  is the temperature,  $\Delta G^0$  is the Gibbs energy,  $\bar{N}$  is the average number of elementary fracture carriers (proportional to the number of defects),  $C$  is a constant.



**Figure 5.** The increase in the entropy of mixing to the number of elements in equimolar alloys in a disordered state (a) [2], the change in the friction coefficient of nickel with different grain sizes (b) [23]

A decrease in the coefficient of friction of the FeCrNiTiZrAl coating is possible due to the effect on the friction process by a change in the Gibbs energy in equation (1). First, the change in the Gibbs energy follows formula (2) and Figure 5.

$$\Delta G^0 = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}. \quad (2)$$

Equation (2) shows that the entropy of mixing for the phases of the solid solution increases from a small value for conventional alloys to a large value for high-entropy alloys of the composition [2]. This is also shown in Figure 5a. Secondly, the size effect plays a significant role in nanostructured materials (Figure 1b). In [23], nanostructured nickel was obtained by electrodeposition and the coefficient of friction for various grain sizes is shown in Figure 5b. Nickel friction coefficient of 0.16 is observed at 8 nm and increases to 0.65 at 61 microns, where the bulk phase already begins.

Within the framework of our model [24], the dimensional dependence of the friction coefficient  $k(r)$  is given by the formula:

$$k(r) = k_0(1 - R(I)/r), \quad (3)$$

where  $k_0$  is the coefficient of friction of the bulk phase,  $R(I)$  is the thickness of the surface layer of the solid, which is given by the formula:

$$R(I) = 0,24 \cdot 10^{-9} \cdot \nu \quad (4)$$

where  $\nu$  is the molar (atomic) volume of the element,  $\nu = M/\rho$ ,  $M$  is the molar mass, and  $\rho$  is the density.

The turbomechanical plant in Karaganda mastered the blades for the T-100/120-130-2 TMZ steam turbine. It is a single-shaft three-cylinder unit with two cogeneration steam extractions (upper and lower) and two exhausts. The application of nanostructured coatings FeCrNiTiZrAl on turbine blades made of steel 20Kh13 was carried out using a magnetron with a target (Figure 1 a). A sample of turbine blades with FeCrNiTiZrAl coating is shown in Figure 6a, and in Figure 6b a sample with TiN coating.



**Figure 6.** Turbine blades coated with FeCrNiTiZrAl (a) and coated with TiN (b).

The microhardness of a turbine blade sample with a titanium nitride (TiN) coating is  $\mu = 910$  HV, that is, slightly more than the FeCrNiTiZrAl coating ( $\mu = 740$  HV, Table 3), but the titanium nitride coating has a friction coefficient of  $k = 0.65$ , that is, 10 times less FeCrNiTiZrAl coatings (table 2). This leads to the fact that the service life of a turbine blade with a FeCrNiTiZrAl coating is 3 times longer than the service life of a turbine blade with a titanium nitride coating. Considering that the cost of titanium nitride coating is 2 times higher than the cost of FeCrNiTiZrAl coating, that is, the economic effect is obvious.

#### 4. Conclusion.

Comparison of tables 2 with table 3 shows that the microhardness of stainless steels is almost 2 times less than the microhardness of the nanostructured FeCrNiTiZrAl coating. This means that the studied coating has a hardness much higher than stainless steels and is less susceptible to wear (that is, destruction of the coating), as evidenced by the comparison of tables 2 with table 4. The destruction of the coating is caused by the appearance of a new surface, which is associated with its surface energy  $\sigma$ .

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