# Microhardness of high-entropy coatings

**Yurov Viktor Mikhailovich**

*Candidate of Physical and mathematical Sciences, Associate Professor*

**Guchenko Sergey Alekseevich**

*Doctoral student PhD*

**Makhanov Kanat Matovich**

*Candidate of Physical and mathematical Sciences, Associate Professor*

*Karaganda University named after E.A. Buketov, Karaganda, Kazakhstan*

***Abstract.*** *The article shows that the hardness of most stainless steels is 2-3 times less than high-entropy coatings, which shows the prospect of their use as parts of various industrial structures. Microhardness of metallic glasses, which have a defect-free base, and do not differ from high-entropy coatings. An equation is obtained in the article, which shows that the destruction of the coating should be determined by the surface energy of the coating. It linearly depends on the hardness of the alloy and the destruction of the coating should decrease with decreasing surface energy without changing the mechanical properties of high-entropy coatings. Its decrease is also associated with the formation of nanostructures and the size dependence of the surface energy.*

***Keywords****: microhardness, high-entropy coating, steel, surface energy, destruction of the coating, nanostructure.*

## Introduction

In high-entropy alloys, as a result of the effect of intense mixing, the entropy contribution increases, which stabilizes the formation of a solid solution with a simple structure [1-3]. Based on Boltzmann's hypothesis on the relationship between entropy and system complexity, the configurational change in entropy $\Delta S_{conf}$ during the formation of a solid solution of n elements with equiatomic content can be calculated using the following formula:

$$\Delta S_{conf} = -R \ln(1/n) = R \ln(n), \qquad (1)$$

where R is the universal gas constant, n is the number of mixing elements.

At $n = 5$, $\Delta S_{conf} = 1.61R$ approaches the value of the melting entropy of most intermetallics (about 2R). However, it was later shown that a high entropy of mixing is not a necessary condition for the formation of a single-phase solid solution, but the very term for the name of such an alloy remains in use. We have also investigated high-entropy alloys and coatings obtained by mechanical alloying and magnetron sputtering of targets [4-7].

**Purpose of the study** – let us experimentally investigate the microhardness of high-entropy coatings and propose a model that will allow us to explain the observed effects within the framework of the energy theory..

**Materials and methods**

High-entropy (HEA) coatings of the following composition were used as objects of research: TiNiZrCuCr, CrFeNiTiZrCu, TiFeCuAlSn, AlCrNiTiZrCu, PbCrNiTiZrCu, CrNiTiZrAlCu, made by mechanical alloying [8]. Moreover, after annealing in a vacuum chamber, the samples became nanostructured. In fig. 1a shows, as an example, the samples under study, in Fig. 1b their SEM image, and in Fig. 1c diagram of the formation of nanostructured coatings [9].
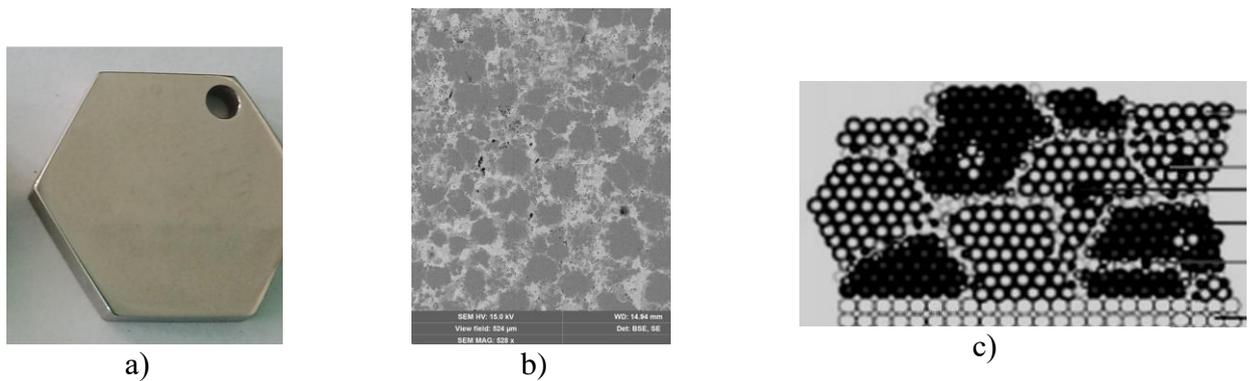


a)                                   b)                                   c)

Figure 1 - Sputtered samples (a), REM samples (b), formation

nanostructured coatings [9].

The roughness of the coating as an example, measured on a JSPM-5400 atomic force microscope (AFM) manufactured by JEOL, is also negligible (Figure 2) [10].



a)                                                       b)
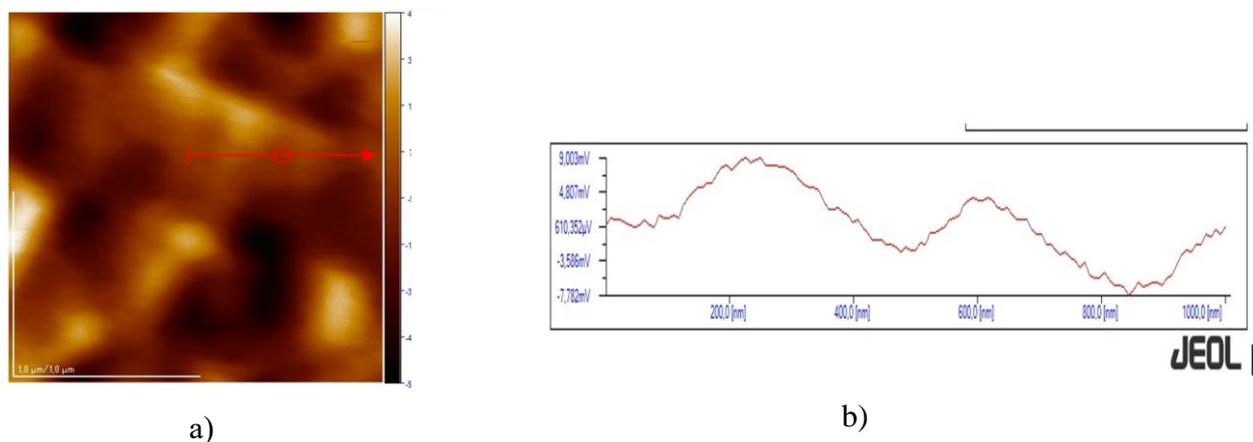
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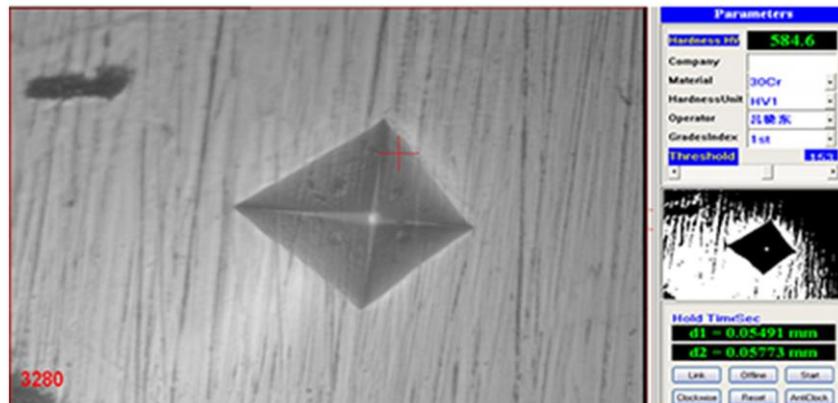


Figure 3 - Microhardness tester HVC-1000A

To determine the specific surface energy (surface tension) σ, we used the method described by us in [11]. The first method provides for the measurement of surface tension by determining the dependence of the microhardness on the thickness of the deposited coating. The dependence of the microhardness of the deposited coating on its thickness is described by the formula:

$$\mu = \mu_0 \cdot (1 - d/h), \tag{2}$$

where μ is the microhardness of the deposited coating; $\mu_0$ - "thick" sample; h is the thickness of the deposited coating. The parameter d is related to the surface tension σ by the formula:

$$d = 2\sigma\upsilon/RT, \tag{3}$$

where σ is the surface tension of a massive sample; υ is the volume of one mole; R is the gas constant; T is the temperature.



a)                                         b)
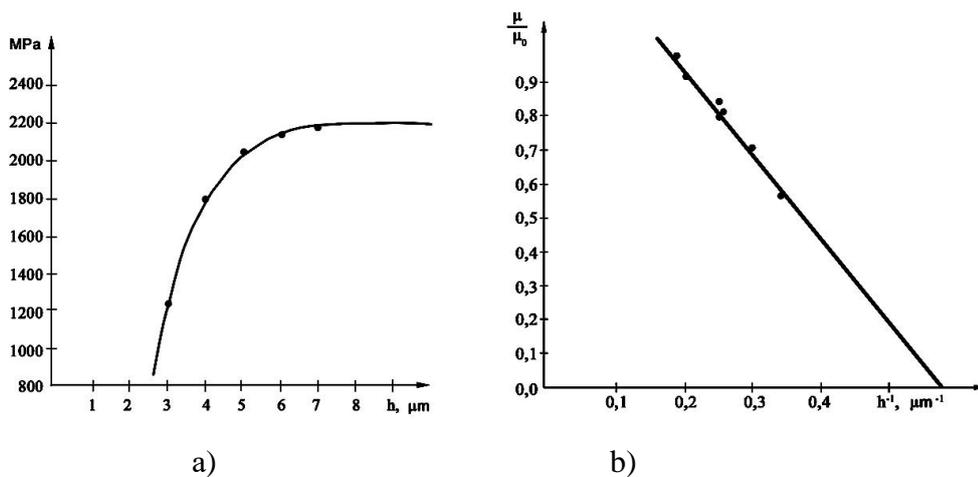
Figure 4 - Dependence of microhardness on the thickness (a) and inverse thickness (b) of the CrFeNiTiZrCu coating on steel 20X13 [11]

As an example, consider the determination of the surface tension of the CrFeNiTiZrCu coating on steel 20X13. The results are shown in Figure 4. In the coordinates $\mu/\mu_0 \sim 1/h$, the experimental curve is straightened in accordance with formula (2), giving the value h = 1.3 μm. For the CrFeNiTiZrCu coating on 20X13 steel, the surface tension obtained is $\sigma$ = 1.409 J/m$^2$. This value confirms the wear resistance of the CrFeNiTiZrCu coating on steel 20X13.

**Results and discussion**

Using the above methods, a table of experimental values can be given.

Table 1 shows that pentaatomic alloys have high hardness, surface energy ranges from 1 to 1.2 J/m$^2$. Hexaatomic alloys have slightly less hardness. Let us compare the hardness of stainless steels [12] with the hardness of high-entropy coatings from Table 1.

Table 1 - Experimental properties of high-entropy coatings (HEA) and metallic glasses (MS) [13]

| HEA | $\mu$, HV | $\sigma$, J/m$^2$ | MS | $\mu$, HV |
|---|---|---|---|---|
| CrTiNiZrCu | 890 | 1.149 | $Fe_{78}Mo_2B_{20}$ | 1015 |
| TiFeCuAlSn | 700 | 1.192 | $Fe_{40}Ni_{40}P_{14}B_6$ | 640 |
| CrFeNiTiZrCu | 740 | 1.409 | $Fe_{78}P_{13}C_7$ | 760 |
| AlCrNiTiZrCu | 585 | 1.644 | $Fe_{78}Si_{10}B_{12}$ | 890 |
| PbCrNiTiZrCu | 560 | 1.387 | $Ni_{75}Si_8B_{17}$ | 860 |
| CrNiTiZrAlCu | 530 | 1.152 | $Co_{75}Si_{15}B_{10}$ | 910 |

Table 2 - Hardness of stainless steels [12]

| Steel | $\mu$, HV | Steel | $\mu$, HV |
|---|---|---|---|
| 12X13 | 121-187 | 08X17T | 372 |
| 40X13 | 143-229 | 10X17H13M2T | 200 |
| 08X18H10 | 170 | 12X18H10T | 179 |

The hardness of most stainless steels is 2-3 times less than high-entropy coatings, which shows the prospect of their use as parts of various industrial structures. For comparison, Table 1 shows the microhardness of metallic glasses, which have a defect-free base and do not differ much from high-entropy coatings [13]. What is the reason for this difference?

We will consider the question of the response of a subsystem of n electrons in high-entropy alloys to an external action during friction from the standpoint of nonequilibrium statistical thermodynamics. The electrons in the alloy will be considered as a system of non-interacting

particles immersed in a thermostat. The thermostat is a metal alloy minus n "free" electrons. Quantum transitions during friction, caused by the interaction of a system of electrons with a thermostat, will be dissipative (with probability P), in contrast to the interaction during friction (with probability F). Dissipative processes lead to the fact that the secondary field (system response) is always less than the primary one, which causes the formation of heat during friction.

We will assume that the electron subsystem exchanges only energy with the thermostat during friction. Then the corresponding ensemble of particles will be canonical. In this case, the expression for the statistical entropy is:

$$S = -k \sum_i f_i \ln f_i, \tag{2}$$

where $f_i$ is the distribution function; k is Boltzmann's constant.

Differentiating (2) in time and transforming, we get:

$$\frac{dS}{dt} = \frac{k}{2} \sum_{i,j} \left( \ln f_i - \ln f_j \right) \left( P_{ij} f_i - P_{ji} f_j \right), \tag{3}$$

where $P_{ij}$ is the probability of transition from the initial i (with energy $E_i$) to the state j excited by friction (with energy $E_j$). For dissipative processes, the principle of detailed balance has the form:

$$\frac{g_i P_{ij}}{g_j P_{ji}} = e^{\frac{E_j - E_i}{kT}}, \tag{4}$$

where $g_i$, $g_j$ are statistical weights for the levels $E_i$ and $E_j$. Then (4) takes the form:

$$\frac{dS}{dt} = \frac{k}{2} P_{ij} \left( \ln f_i - \ln f_j \right) \left( f_i - \frac{g_i}{g_j} f_j e^{-\frac{E_i - E_j}{kT}} \right), \tag{5}$$

Canonical distribution function:

$$f_{ij} = \frac{1}{Z} e^{-E_{ij}/kT}$$

where the statistical sum:

$$Z = e^{-G/kT}$$

where G is the Gibbs potential (free energy) of the thermostat + electron system.

We assume that the non-configurational part of the Gibbs potential linearly depends on the concentration of n electrons:

$$e^{-G/kT} = \sum_N h(n), \tag{6}$$

where $h(n) = \omega(n) \cdot e^{-G/kT}$; $\omega(n)$ - statistical weight.

After cumbersome but simple calculations, it is easy to show that the function $h(n)$ is a Gaussian distribution about a value with low variance, i.e.:

$$h(n) = h(\bar{n})e^{-\Delta\bar{n}^2/n} \tag{7}$$

Substituting (7) into (6), we have:

$$e^{-G/kT} = h(\bar{n})\sum_{\Delta n} e^{-\Delta\bar{n}^2/\bar{n}} \tag{8}$$

To estimate the sum in (8), we replace it by the integral:

$$\sum_{\Delta n} e^{-\Delta\bar{n}^2/\bar{n}} = \int_{-\infty}^{+\infty} e^{-x^2/\bar{n}}dx = \sqrt{\pi x} \tag{9}$$

Then (8) takes the form:

$$e^{-G/kT} = h(\bar{n})(\pi\bar{n})^{1/2}. \tag{10}$$

Taking the logarithm of (10), we get:

$$G/kT = -\ln\omega(\bar{n}) + \frac{G(\bar{n})}{kT} + \frac{1}{2}\ln(\pi\bar{n}) \tag{11}$$

where $G(\bar{n})$ is the part of the total Gibbs potential associated with the electron concentration. From the estimate of the first logarithmic term it follows:

$$\ln\omega(\bar{n}) = n\ln\left(1 + \frac{\bar{n}}{n}\right) + \bar{n}\ln\frac{n+\bar{n}}{n} \tag{12}$$

Approximating the logarithm in the first term on the right-hand side of (12) by the first term of its expansion in a series, and expressing the second term in terms of the Gibbs potential of the thermostat $G^f$, we obtain:

$$\ln\omega(\bar{n}) = \bar{n} + \bar{n}G^f/kT \tag{13}$$

Substituting (13) into (11) and neglecting the $1/2\ln(\pi\bar{n})$ term in comparison with $\bar{n}$, we obtain:

$$G = G(\bar{n}) - \bar{n}G^f - \bar{n}kT. \tag{14}$$

As above, assuming that the thermodynamic potential $G(\bar{n})$ depends on the equilibrium number of electrons $G^f$ in a linear manner, i.e:

$$G = G^0 + \bar{n}G^f, \tag{15}$$

where $G^0$ is the thermodynamic potential of the thermostat, we find:

$$G = G^0 - \bar{n}kT. \tag{16}$$

With the help of (16), the expression for Z is transformed to the form:

$$Z = e^{-G^0/kT}e^{\bar{n}}. \tag{17}$$

Substituting (17) into (5), we find:

$$\frac{dS}{dt} = \frac{k}{2}\sum_{i,j} P_{ij} e^{G^0/kT} e^{-\bar{n}} e^{-E_i/kT} \left(\frac{E_j - E_i}{kT}\right)\left(1 - \frac{g_i}{g_j} e^{2\frac{E_i - E_j}{kT}}\right). \tag{18}$$

Neglecting small terms and replacing the sum by an integral in (18) (which is true for the continuous spectrum of electron energies in the alloy), we obtain:

$$P = \frac{2\Delta S}{k\Delta t}\exp\left\{-\frac{E_m - G^0/\bar{n}}{kT}\right\}, \tag{19}$$

where $\Delta S$ is the change in entropy in the dissipative process; $E_m$ is the average value of the energy of the ground state of electrons during friction; $\Delta t$ is the time of movement during friction.

The response function of the thermostat + electrons system is:

$$\Omega = \frac{F}{F+P} = \frac{1/\tau}{1/\tau + 2\Delta S/k\Delta t \exp\left\{-(E_m - G^0/\bar{n})/kT\right\}}, \tag{20}$$

where F is the probability of a quantum transition inducing a secondary field of electrons, and F = $1/\tau$ is the "radiative" lifetime of the electron system in an excited state during friction.

From (20), we obtained the following formula for the destruction efficiency $\Omega = \eta$ of a metal coating:

$$\eta = \frac{k^2\Delta t}{2\Delta S \cdot \tau} \cdot T \cdot \frac{E_m}{G^0} \cdot \bar{n} = \text{const} \cdot T \cdot \frac{\sigma \cdot S}{\tau \cdot G^0} \cdot \bar{n}, \tag{21}$$

Equation (21) describes the destruction of the coating $\eta$ proportional to k - the Boltzmann constant, the change in entropy $\Delta S$ and the time of motion during friction $\Delta t$, the work of friction forces $E_m = A = \sigma S$, the concentration of electrons n near the Fermi level, surface energy $\sigma$, contact area S and vice versa is proportional to the relaxation time $\tau$ and the Gibbs energy $G^0$ of the thermostat.

For high-entropy coatings $G^0 = H\text{-}TS + PV \rightarrow S \sim 2R$ and the destruction of the coating should decrease. The surface energy $\sigma$ linearly depends on the hardness of the alloy: $\sigma = \alpha \mu$, $\alpha = $ const, and the destruction of the coating should decrease with a decrease in the surface energy.

Its decrease is also associated with the formation of nanostructures and the dependence of the surface energy $\sigma$ according to A.I. Rusanov. [15]: $\sigma = K r \rightarrow 0$ at $r \rightarrow 0$ (see Figure 1c).

**Conclusion**

The method of mechanical alloying for obtaining high-entropy coatings is much cheaper than the method of metallurgy, which produces cast high-entropy ingots. The hardness of high-entropy coatings is 2-3 times higher than the hardness of stainless steels, but it turns out to be similar to the hardness of metal glasses, which are also quite difficult to obtain.

We have shown experimentally and theoretically that the destruction of high-entropy coatings is mainly determined by the surface energy, which is proportional to the hardness of the coating. The surface energy for the coating decreases due to its nanostructural state, without significantly changing its physical properties. The destruction of high-entropy coatings is also reduced due to an increase in the entropy of the coating.

**Thanks**

# References

*1.	Yeh J.-W., Chen S.-K., Lin S.-J., Gan J.-Y., Chin Ts.-Sh., Shun T.-Ts., Tsau Ch.-H., Chang Sh.-Y. Nanostructured High-Entropy Alloys with Multiple Principle Elements: Novel Alloy Design Concepts and Outcomes // Advanced Engineering Materials, 2004, Vol. 6, №8. - P. 299-303.*

*2.	Yeh J.W., Chen Y.L., Lin S.J. High-entropy alloys – a new era of exploitation // Materials Science Forum, 2007, Vol. 560. – P. 1-9.*

*3.	Wang Y.P., Li B.Sh., Heng Zh.F. Solid Solution or Intermetallics in a High-Entropy Alloy // Advanced Engineering Materials, 2009, Vol. 11, № 8. – P. 641-644.*

*4.	Yurov V.M., Eremin E.N., Guchenko S.A. Wear resistance and tribological properties of high entropy coatings CrNiTiZrCu // Eurasian Physical Technical Journal, 2020, Vol.17, No.1 (33). – P. 13-18.*

*5.	Yurov V.M., Guchenko S.A., Makhanov K.M. Structural properties of the high-entropy TiNiZrCuCr coating // Modern science-intensive technology, 2020, No. 4. - P. 78-83.*

*6.	Yurov V.M., Shelpyakov B.N., Guchenko S.A., Tvardovsky A.N. Application of high-entropy coatings on turbine blades // Trends in the development of science and education, 2020, No. 59, Part 1.- P. 49-54.*

*7.	Yurov V.M., Goncharenko V.I., Oleshko V.S. Anisotropy of surface energy and thickness of the surface layer of magnetic nanostructures // Nano- and microsystem technology, 2021, V. 23, No. 2. - P. 59-62.*

8.      *Yurov V.M., Guchenko S.A., Tvardovsky A.N. Two targets for magnetron deposition of high-entropy coatings // Trends in the development of science and education, 2020, no. 60(1). - P. 28-34.*

9.      *Pogrebnyak A.D., Bagdasaryan A.A. Pink A.V., Dyadyura K.A. Multicomponent nanocomposite coatings with adaptive behavior in surface engineering // Uspekhi fizicheskikh nauk, 2017, Vol. 187, no. 6. - P. 629-652.*

10.      *Yurov V.M., Guchenko S.A., Makhanov K.M. Atomic force microscopy of high-entropy coatings // International Journal of Applied and Fundamental Research, 2020, no. 4. - P. 62-67.*

11.      *Yurov V.M., Laurinas V.Ch., Guchenko S.A., Zavatskaya O.N. Surface tension of hardening coatings // Hardening technologies and coatings, 2014, No. 1. - P. 33-36.*

12.      *Povolotskiy D.Ya., Gudim Yu.A. Stainless steel production. - Chelyabinsk: SUSU Publishing House, 1998. - 236 p.*

13.      *Cheng Y.Q., Ma E. Atomic-level structure and structure–property relationship in metallic glasses // Progress in Materials Science, 2011Vol. 56. – P. 379–473.*

14.      *Yurov V.M., Guchenko S.A., Zavatskaya O.N. Structure and surface tension of composite coatings // Bulletin of KSU. Physics, 2012, No. 1 (65). - P. 45-53.*

15.      *Rusanov A.I. Phase equilibria and surface phenomena. - Publishing house "Chemistry", Leningrad branch, 1967. - 388 p.*