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Structure and Physical Properties of High Entropy Coatings on Surfaces of Weapons and Military Equipment Parts

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Abstract. The method of spraying CGDN coatings we propose is universal for repairing military equipment in the field. We carried out the method using a Dimet-425 installation and an IPG Photonics laser. The increase in heat resistance and adhesion of the coated sample relative to the uncoated sample is explained by the fact that the modified surface layer of the sample is a transition layer that has a sharp boundary with the base material or transition zone, consisting of a diffusion zone and a thermal-affected zone. The characteristic adhesion value obtained for CGDN coatings is 20 - 80 MPa, and the powder utilization rate reaches 50 - 80%.

Keywords: coating, sputtering, laser, particle speed, particle impact, deformation, adhesion.

Introduction

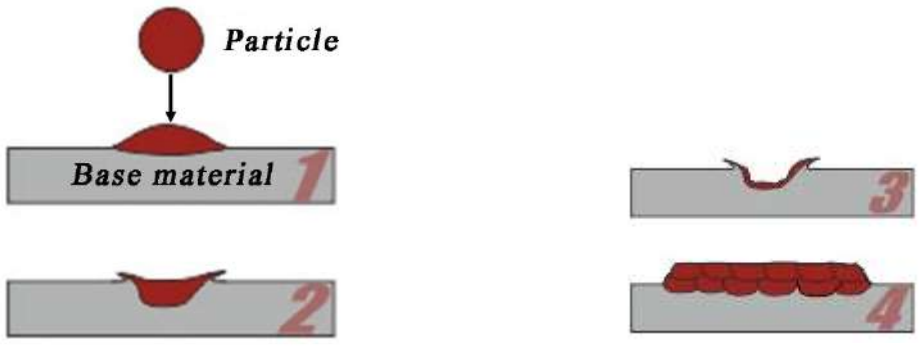
In 2008, the MIL-STD-3021 standard "Sputtering of materials. Cold gas dynamic spraying", which describes the process of operation of the CGD method, as well as methods for testing coatings and is used in the restoration of military equipment using CGD [1]. This area of coating is also being explored by developers from Japan, the Republic of Korea, India, Austria and Australia [2]. A review of high-entropy (HEC) coatings on parts of various industries, including aviation, rocket and military equipment, has been carried out in recent years in reviews [3-7]. To increase the service life of both artillery and small arms barrels, coatings are used, most often chromium with a thickness of 50 to 180 microns, which increases the service life by 2.5-3 times [8-10] - for example, for small arms from conventional 10 thousand to 25-30 thousand shots. To increase the wear resistance of barrels, chemical-thermal treatment of the inner surface, in particular nitrocarburization, is also used [11].

In this article we will consider the structure and physical properties of high-entropy coatings on the surfaces of weapons and military equipment.

1. Methodology

Research on the application of coatings using the cold gas dynamic spray (CGDN) method began in the first half of the 1980s. In the period from 1980 to 2022, more than 200 patents were received for various design modifications of spraying installations, as well as in the field of applying metal coatings for various functional purposes. The main energy source in the processes of formation of CGDN coatings is the kinetic energy of high-speed particles in the solid phase. The main physical mechanism of CGDN is the high-speed deformation of sprayed particles upon impact, leading to intense shear flows of the material along the contact boundaries and the formation of adhesive-cohesive bonds. As a result of experiments, coatings of almost all types of metals (Al, Cu, Zn, Mo, Ta, Ti, Cr, Nb, Zr, Ag, Fe and many others) and alloys widely used in industry were successfully applied [12-14] .

Before moving on to our technology, let's consider the interaction of particles with the base, which we will further represent as military steel (Fig. 1).



a) b)

Fig. 1. - Effect of particle velocity on coating quality

Scheme in Fig. 1 boils down to this:

1. The coating particle has reached the minimum impact speed, which is necessary to excite the mechanism of interaction with the surface of the substrate (processed sample). This so-called “critical speed” affects the properties of the coating material.

2. Since the impact speed is higher than the critical speed, the deformation and quality of adhesion of the particles increase.

3. If the impact velocity is too high (the "erosion rate"), more material is destroyed than added. No coating is formed.

4. In order for a dense and formed coating to form, the particle impact velocity value must be between the values of the critical velocity and the erosion rate.

We applied HES coatings using the CGDN method with a supersonic supply of a gas-powder mixture using the Dimet-425+Laser installation (Fig. 2). The installation included an IPG Photonics fiber laser with a wavelength of 1064 nm and a maximum power of 6 kW. The installation of HES coatings using the CGDN method (Fig. 2) contains a chamber 1, a nozzle 2, a substrate 3 for supplying a gas-powder mixture, and a laser 4.

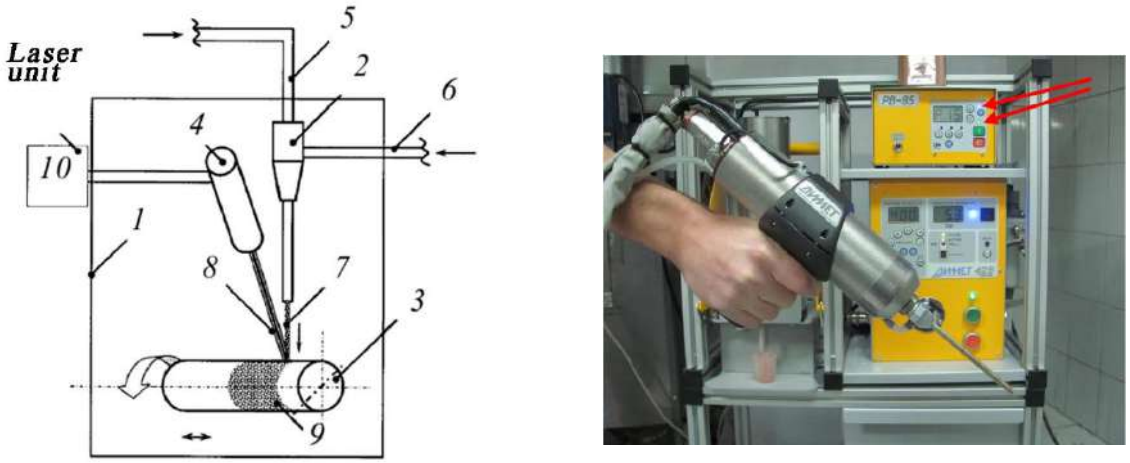


Fig. 2. - Installation of HES coatings using the CGDN method (left); powder feeder from the Dimet-425 installation (right)

Nitrogen is supplied to spray nozzle 2 using pipe 5, and powder is supplied to spray nozzle 2 using pipe 6. The gas-powder mixture 7 emerging from the nozzle 2 and the laser beam 8 are directed to the surface 9 of the substrate 3. The laser unit 10 is an electronic unit that controls the power of the laser radiation of the laser 4. Movement can be carried out, for example, manually or mechanically using gear or worm mechanisms transfers. Mechanically, the transmission moves the substrate 3 relative to the spray nozzle 2. As a result, a coating 9 is formed on the surface of the substrate 3. During the application of the gas-powder mixture 7, the substrate moves mechanically using gear mechanisms. One of the main features of the device is the ability to change the angle of inclination of the laser head, as well as shift the focus of the laser spot relative to the focus spot of the powder on the surface of the sample. The device we assembled based on the Dimet-425 installation is similar to the installation described in the Patent [15]. A similar installation is proposed in the Patent [16].

Results and discussion

In the works listed above, it was found that such criteria as the critical speed in the gas jet, the flow rate, and the speed of the sprayed particles increased. Also, the issue of the influence of particle speed in the CGDN process on the number of fixed powder particles when interacting with an obstacle was considered. In [2], it was found that an increase in the spraying speed to 780 m/s leads to the formation of not only craters from rebounded powder particles, but also to the fixation of the powder material, and a subsequent increase in the speed of the part to 850 m/s when using pure helium contributes to an increase the proportion of fixed parts is up to 0.5. An analysis of the nature of particle deformation at different deposition rates showed that an increase in the speed of particle movement leads to the ejection of metal along the periphery.

It turned out that by increasing the particle consumption it is possible to switch from substrate erosion to deposition. The main features of the spraying process in the mode of low impact speeds are the presence of a critical particle flow rate Qi, below which a coating is not formed at any time of exposure to a two-phase jet, as well as a very low value of the spraying coefficient $\Delta m/M = 10^{-3} \div 10^{-4}$. In addition, coatings obtained in this mode differ significantly in their properties from coatings obtained at $\upsilon_h > \upsilon_g$. At $\upsilon_{ch} < \upsilon_g$, when single particles are not fixed on the substrate, the process of formation of coatings at sufficiently high particle flow rates $Q_i > Qi_п$ can be explained by an increase in the temperature of the substrate surface due to heat release during particle impacts, activation of the substrate surface, as well as the presence of the effect of particle interaction - double impacts. The optimization calculations carried out confirmed the fairly high efficiency of using nozzles with a critical section size of 2 - 3 mm

and a length of 100 - 200 mm to accelerate particles 5-30 microns in size, which are poured into the hopper of the Dimet-425 installation in the amount of 80-100 g (Fig. 2b).

It is easier to judge the surface of military equipment from the AFM images of wind-electronic coatings shown in Fig. 3.

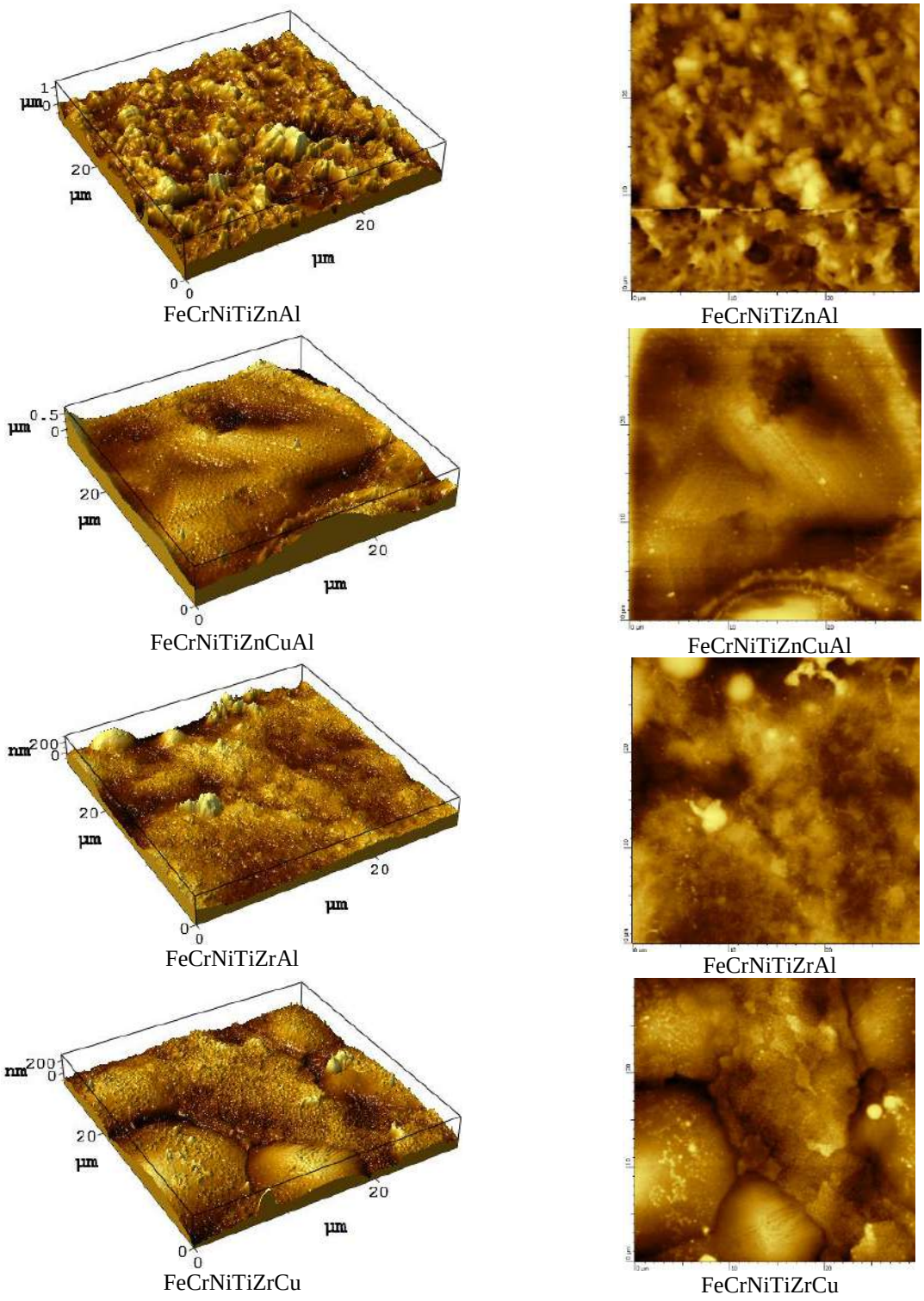
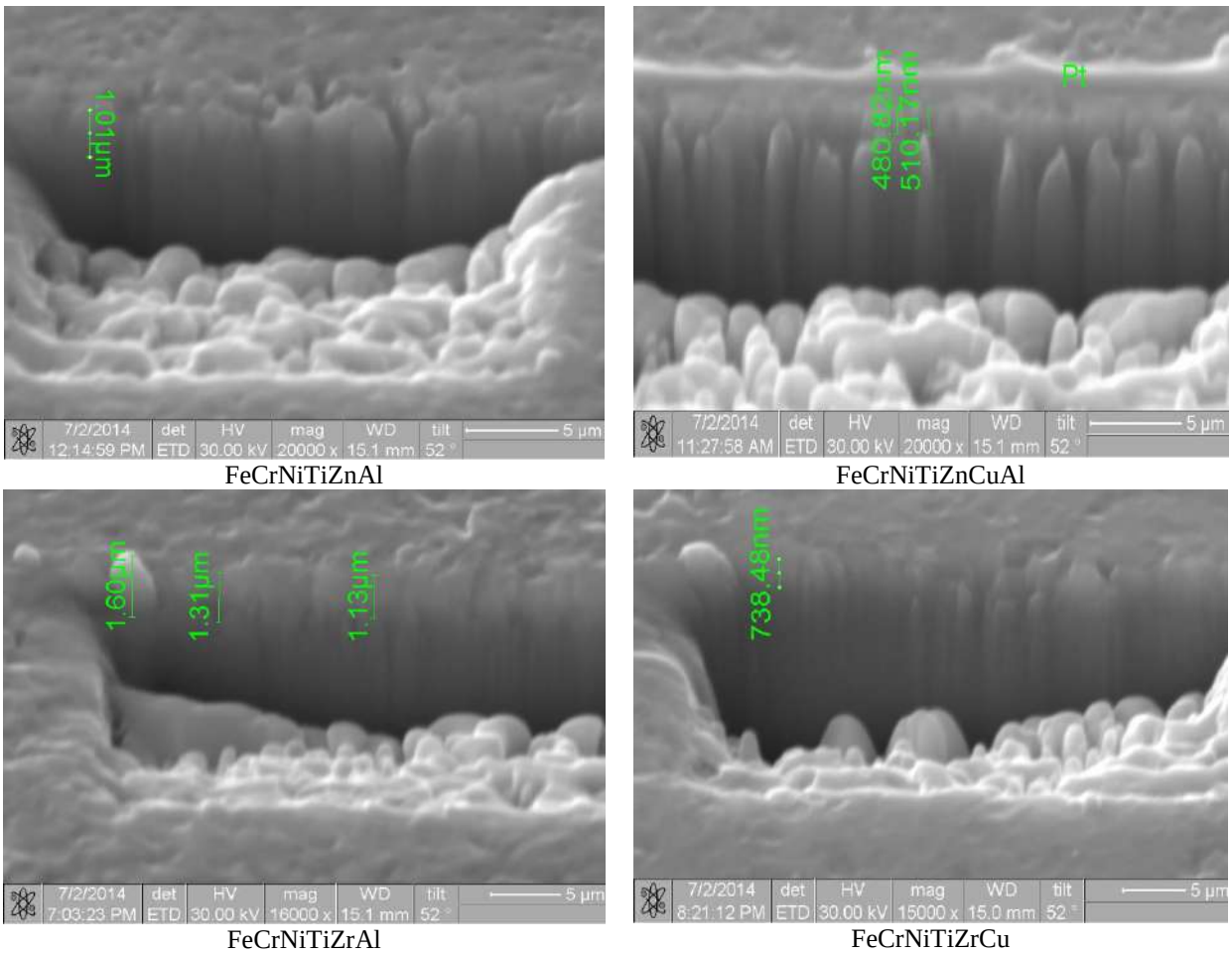


Fig. 3. - AFM images of HES coatings in 3D and 2D projections

Let us now cut the coverings in Fig. 3, using the Quanta 200 3D system. In Fig. 3 and 4 show images of a cellular and pencil structure, similar to Benard cells. A special feature of the surface, including multi-element coatings, is the fact that the surface is a nanostructure.

For the surface, surface energy σ (J/m^2) plays a significant role, determining such an important characteristic of the coating as adhesion energy, which is responsible for the destruction of the coating.



FeCrNiTiZnAl FeCrNiTiZnCuAl

FeCrNiTiZrAl FeCrNiTiZrCu

Fig. 4. - Cutting of HES coatings

The intensity of material destruction is determined by the adhesion energy at the interface:

$$W_{à} = 2\sigma \cdot S \ \ [J/m^2]$$

Here S is the surface area of the sample. Table 1 presents the adhesion energy for the coatings shown in Fig. 3 or 4. We determined the surface energy σ using the method described in [17]. The essence of this method was the dimensional dependence of the thickness of the coating on its microhardness or some physical property, for example, the resistivity of the coating.

Table 1. Surface energy and coating adhesion energy

Coating	σ, J/m^2	W$_a$, J/m^2
FeCrNiTiZnAl	1.05	2.10
FeCrNiTiZnCuAl	1.16	2.32
FeCrNiTiZrAl	1.17	2.34
FeCrNiTiZrCu	1.19	2.38

When the coating is formed, internal stress-strain states (SSS) arise in it. In a coating, SSS creates an energetic state that prevents adhesion and promotes peeling of the coating. SSS energy can be estimated using the formula [18]:

$$W_{SSS} = (\sigma_{SSS}^2 / 2Å) \cdot S \cdot h \, .$$

Here σ_{SSS} is the internal stress (Pa), E is Young's modulus (Pa), h is the coating thickness. Let us estimate W_{SSS} according to the data in Fig. 3, and take the coating thickness h from Fig. 4. Let's take Young's modulus from steel 12X18H10T – E = 205 10^9 Pa, h = 7 10^{-6} m, $\sigma_{SSS} \approx 1\ 10^9$ Pa, then we get $W_{SSS} \approx 0.02$ (J/m^2). This means that our coating Wa >> W_{SSS} is much greater than the energy of coating separation.

We carried out heat resistance tests in accordance with GOST 6130-71. Before testing, all test samples were thoroughly cleaned. The heat resistance tests themselves were carried out in electric resistance furnaces of the G-30 type in an air atmosphere, with automatic temperature control with an accuracy of ±10 °C. During the tests, special ceramic crucibles were used. The samples were placed in a crucible, which was then sent into a furnace. Heat resistance was assessed by the mass of oxidized material. Weighing of samples before and after heat treatment was carried out on an analytical balance with an accuracy of 0.1 mg. The research results are presented in table 2.

Table 2. Loss of coating mass after heat treatment at 1100 °C

Coating	Mass of oxidized coating, mg	Coating	Mass of oxidized coating, mg
Sample without coating, steel 12X18H10T	56,8	FeCrNiTiZrAl	5,4
FeCrNiTiZnAl	14,4	FeCrNiTiZrCu	4,1
FeCrNiTiZnCuAl	6,6	-	-

From Table 2 it follows that the highest heat resistance of the coatings we studied is the FeCrNiTiZrCu coating, and the lowest is FeCrNiTiZnAl. The increase in heat resistance of a coated sample relative to an uncoated sample is explained by the fact that the modified surface layer of the sample is a transition layer, which has a sharp boundary with the base material or transition zone, consisting of a diffusion zone and a heat-affected zone. The transition layer is formed both by the direct transfer of material during CGDN to the substrate, and as a result of the chemical interaction of the coating and substrate materials with each other and with the environment. The transition layer obtained as a result of CGDN on a steel substrate contains austenitic and martensitic phases, carbides, nitrides, intermetallic compounds, oxides of the base and alloying electrode. Coatings formed by FeCrNiTiZrCu form unlimited solid solutions with the substrate and are characterized by high continuity and low porosity. And most importantly, the transition layer formed by these metals and the substrate, after laser exposure, remains practically unchanged.

The use of preliminary (before CIB) thermal activation of the surface makes it possible to increase the adhesion of the coating to the base and increase the homogeneity of its structural structure. As a result, the increase in weight gain due to oxidation is minimal. This fact allows us to conclude that surface activation is an important part in the technological process of producing HE coatings.

If we compare the values in Table 2 with Table 1, we come to the conclusion that a heat-resistant coating also corresponds to a high surface energy.

The wear resistance of coated parts was identical: for cutting tools, which was ensured by testing in the CNC machine shop using the same machining programs. The test results are shown in Table 3.

Table 3. Increase in wear resistance of coatings I%

Coating	I%	Coating	I%
FeCrNiTiZnAl	15	FeCrNiTiZrAl	40
FeCrNiTiZnCuAl	25	FeCrNiTiZrCu	65

If we compare the values in Table 3 with Table 1, we come to the conclusion that a wear-resistant coating also corresponds to a high surface energy.

Conclusion

The highest heat resistance of the coatings we studied is the FeCrNiTiZrCu coating, and the lowest is FeCrNiTiZnAl. The increase in heat resistance of a coated sample relative to an uncoated sample is explained by the fact that the modified surface layer of the sample is a transition layer, which has a sharp boundary with the base material or transition zone, consisting of a diffusion zone and a heat-affected zone.

The use of preliminary (before CIB) thermal activation of the surface makes it possible to increase the adhesion of the coating to the base and increase the homogeneity of its structural structure. As a result, the increase in weight gain due to oxidation is minimal. This fact allows us to conclude that surface activation is an important part in the technological process of producing HES coatings.

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