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E. S. Platonova[1],
G. S. Zhetesova[1]**, Dr. Sci. (Tech.), Professor,**
V. M. Yurov[2]**, Cand. Sci. (Phys.-Math.), Assoc. Prof.,**
S. A. Guchenko[2]

1 – Karaganda State Technical University, Karaganda, Kazakhstan
2 – Karaganda State University named after E. A. Buketov, Karaganda, Kazakhstan, e-mail: exciton@list.ru

ANTICORROSION AND STRENGTHENING COATINGS FOR MINING EQUIPMENT

Є. С. Платонова[1],
Г. С. Жетесова[1]**, д-р техн. наук, проф.,**
В. М. Юров[2]**, канд. фіз.-мат. наук, доц.,**
С. А. Гученко[2]

1 – Карагандинський державний технічний університет, м. Караганда, Казахстан
2 – Карагандинський державний університет ім. Е. А. Букетова, м. Караганда, Казахстан

АНТИКОРОЗІЙНІ ТА ЗМІЦНЮЮЧІ ПОКРИТТЯ ДЛЯ ГІРНИЧОШАХТНОГО УСТАТКУВАННЯ

Purpose. To clarify the dependence of the corrosion resistance and durability of coatings on their basic physical properties on the basis of a thermodynamic model. To carry out an experimental study of corrosion and strength characteristics of multi-coatings covering the parts of mining equipment.

Methodology. Elementary carriers of corrosion, thermal and brittle fracture are considered as a system of non-interacting particles immersed in a thermostat. The response function of the subsystem of elementary carriers of the destruction to the external field was derived through the methods of nonequilibrium statistical thermodynamics.

When coating, the cathodes prepared by induction melting were used. The quantitative analysis of the elemental composition of composite cathodes was held with the JEOL JSM-5910 electron microscope. To measure the microhardness the HVS-1000A micro durometer was used. Determination of corrosion rate in different technological environments was conducted in accordance with GOST 9.908-8512. To determine the corrosion resistance of the coatings we used the method of anodic polarizing initiation of defects (APID).

Findings. A relation between the rate of corrosion, the surface tension of metal coatings and their melting point was obtained. The formula describing the strain state of a rigid body, including the area of destruction, was derived. The corrosion resistance and strength characteristics of composite coatings on parts of mining equipment were experimentally determined.

Originality. The dependence of the corrosion resistance, durability of coatings on their surface tension and melting point was obtained.

Practical value. The resulting formula can be used for qualitative analysis and prediction of the rate of destruction and metal coatings under corrosion, deformation and thermal influences.

Keywords: *nonequilibrium statistical thermodynamics, response function, coating, corrosion, fracture, deformation, strength, microhardness*

Statement of the problem. Corrosive properties of mine waters are associated with the presence of sulfur, iron sulfate, magnesium and aluminum in coal and other bulk. This is characteristic of all coal basins of the world. Pumping mine water from mine workings leads to corrosion of metal parts of pumps, pipes, valves, etc. The shaft lining, which is also in strain-stress state under the influence of rock pressure, undergoes considerable corrosion as well.

In addition to corrosive wear, parts of treatment and tunneling machines and plows are subjected to high mechanical wear because of the large hardness of coal bearing rocks.

As early as in the 80s of the last century, it became clear that instead of developing special steels and alloys, it was necessary to create a various technologies applying super hard, corrosion-resistant coatings for machine parts and machines working in extreme conditions.

New impetus to the development of research in this direction is associated with the development of nanotechnologies and, in particular, with the development of vacuum deposition methods for nanocrystalline coatings possessing sometimes unique physical properties that are difficult to reach by conventional methods of metallurgy.

Thus, the problem of developing the technologies of applying strengthening, anti-corrosion and other functional coatings is topical for many industries, including mining.

Analysis of the recent research and publications. Regarding the preparation of nanostructured superhard coatings, the most promising methods are those of vacuum ion-plasma: magnetron sputtering, ion and vacuum arc deposition. This is because apart from thermal factors, the-re are others including a high degree of ionization, energy density and flux particles. In recent years, to produce nanocrystalline coatings, multi (multielement) plasma flows were used [1–7].

The main advantage of these methods is the possibility of creating a very high level of physical and mechanical properties of materials in thin surface layers, deposition of dense coatings of refractory chemical compounds as well as diamond-like, which cannot be obtained by conventional methods.

However, in most cases, the synthesis of different elemental composition of the coating is carried out based on intuitive considerations without applying model representations.

The aim of this work is to develop models of corrosion and mechanical failure of metals, alloys and metallic coatings, as well as a pilot study of corrosion and mechanical properties of multi-coatings obtained by the ion-plasma method while spraying composite cathodes.

The main material. ***Thermodynamic model of corrosion and mechanical failure of metals, alloys and coatings.***

Considering the elementary carriers of corrosion or mechanical damage as a subsystem of non-interacting particles immersed in a thermostat, it is possible to obtain the response function of this subsystem to the external action based on quantum statistical thermodynamics [8]. If the area of corrosion spots S is assumed to be the response function, we obtain the following

$$S = \frac{kT}{C} \cdot \frac{A}{G^0} \cdot \overline{N} \cdot t, \qquad (1)$$

where A is the work of 'external forces' T is the temperature; G^0 is Gibbs potential of a bulk sample of metal; $\overline{N}$ is the average number of points of corrosion; t is time-to-corrosion; k is the Boltzmann constant; C is the constant.

The work of 'external forces' is equal to the change of the standard thermodynamic potential ΔG_T, which is the basis of thermodynamics and corrosion can be determined through the chemical equilibrium constant K_p according to the formula [9]

$$\Delta G_T^0 = -RT 2{,}303 \lg K_p. \qquad (2)$$

Corrosion starts from the surface layer and therefore in the (1) it is necessary to make a replacement $G^0 = \sigma \cdot S_0$ – where σ is the surface tension; S_0 is the specific surface. As shown in [10], the surface tension of the metal is related to its melting point ratio $\sigma = 10^{-4} \cdot T_p$.

Taking the thickness of the corrosion layer h as a response function in (1), for corrosion rate ($V_c = h/t$) , which is determined experimentally, we finally obtain the following expression

$$v_c = C_1 \frac{T^2 \lg K_p}{\sigma S} = C \cdot \frac{T^2 \lg K_p}{T_p}, \qquad (3)$$

where the constant C includes all the constants of the previous formulas.

Formula (3) can be used to predict the corrosion rate of newly synthesized coatings and to select their elemental composition. For thin films and coatings, surface tension the value of σ is additive and may be determined experimentally as described in [10].

Similarly, the speed of the mechanical or thermal destruction of the coating will have the following relationships

$$v_p = C \cdot \frac{E_F}{Tp}; \qquad (4)$$

$$v_p = C_1 \cdot \frac{\mu}{\sigma}. \qquad (5)$$

Equation (4) is valid for pure metals. Using the experimental values of the Fermi energy E_F, melting and corrosion rates for ten metals *Au, Ag, Al, Cu, Fe, Ni, Pb, Pt, Sn, Zn*, we calculated the constant C. Up to 20 % of it was constant and equal to $(2.5–3.0) \cdot 10^{-4}$.

Equation (5) is valid for multiple and multi-coatings. In this case, it is better to experimentally determine the corrosion rate and the amount of tension as described in [10].

The corrosion resistance of mining equipment components. To determine the corrosion resistance of the coatings, the method of anodic polarizing initiation of defects (APID) is used. For quantitative integral evaluation of the coating quality, the integral quality parameter $K = (Q - Q_1)/Q_0$ is used where Q_0 and Q_1 are amounts of electricity passing through the electrical cell while polarizing uncoated and coated sample surfaces within the potential range from the starting potential of the substrate material dissolution to the potentials (10−40) % smaller than the starting potential.

The upper limit is usually selected from the interval (3−5) B. The K parameter is dimensionless and normalized. The high grade quality of coating corresponds to the value $K = 1$ and $K = 0$ is the lowest quality.

The coating was applied to the following items of mining equipment: rod (steel 40X); pin 12 (steel 35); coupling with sleeve 12 (steel 35); RU11.008-01 coupling (steel 35); cork GVU 30.002 (steel 35); elbow bend 10NG12 (steel 35); right cheek G9.00.18 (steel 3).

The corrosion rates of the titanium nitride surface coatings are given in Table 1. However, the calculation of economic efficiency of the entire production cycle of the application of titanium nitride coatings showed that the price of the above items of mining equipment increased by approximately 20 % compared to the galvanized coating applied electrolytically at the RGTO plant of the Coal Department of *ArcelorMittal* Temirtau JSC.

It should be noted that despite the increase in the cost of coverage, galvanized coating of the RGTO plant appears to be of low grade. Nitriding of parts was conducted according to the methods described above. Table 2 shows the comparative analysis.

Table 1

The corrosion rate of titanium nitride coatings in the technological environment

Technological environment	Concentration (mass)%	Temperature, °C	Corrosion rate mm/year
Nitric acid	80	20	0.01
Sulphuric acid	52	20	0.03
Hydrochloric acid	80	20	0.05

Table 2

Characteristics of various coatings

Part name	Anti-corrosion coating	Coefficient K
Coupling RU 11.008-01, steel 35	Zinc	0.15
Coupling RU 11.008-01, steel 35	Nitrated	0.40
Coupling RU 11.008-01, steel 35	Titanium nitride	0.75

According to Table 2, the technology of vacuum nitriding, though inferior in corrosion resistance to titanium nitride coatings, surpasses the zinc coating considerably. At the same time, the cost of nitrided parts is (10–15) % lower than that of zinc.

In case of small lots of parts, as well as for mission-critical blocks, it is better to use titanium nitride coatings which enhance corrosion resistance and possess high strength. Vacuum nitriding is a cheaper way to increase corrosion resistance. It has distinct advantages over electrolytic zinc and chrome finish. We applied the method of ion plasma coating *Fe–Al–Ti, Zn–Al–Ti, Zn–Cu–Al–Ti*. Table 3 represents their corrosive characteristics.

As it can be seen from Table 3, the proposed coatings are second only to the titanium nitride coating, but they are much cheaper than all the coatings shown in Table 2. The manufacture of such cathodes does not cause any difficulty. The coating thickness is from 2 to 4 microns, so that a cathode can be sufficient for about 12 thousand parts such as coupling 12 c.

Table 3

Characteristics of various coatings

Part name	Anti-corrosion coating	Coefficient K
Nipple 12 steel 35	Fe-Al-Ti	0.47
Coupling 12 c steel 35	Zn-Al-Ti	0.57
Cork GVU 30,002 steel 35	Zn–Cu-Al-Ti	0.61

Strengthening coatings for components of mining equipment. Cathodes made of steel *12X18H10T* and titanium cathodes were used. Simultaneous sputtering of cathodes in the nitrogen atmosphere on the tangential cutters and tunnelling machines RD25-60 was carried out for 40 minutes. To measure the layer thickness of the applied *12X18H10T+Ti* coating, on the surface a pad was cut with a focused ion be-am using an electron microscope 200 Quanta 3D. The layer thickness is 1.5 mm (Fig. 1).

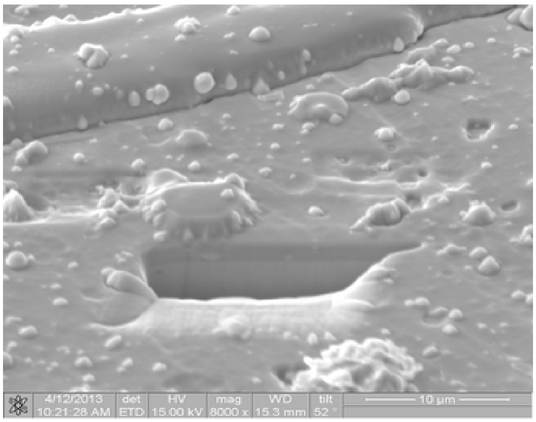

Fig. 1. Thickness of 12X18H10T + Ti coating in the nitrogen gas atmosphere

Fig. 2 shows the elemental composition of the coating, and Table 4 presents the phase composition.

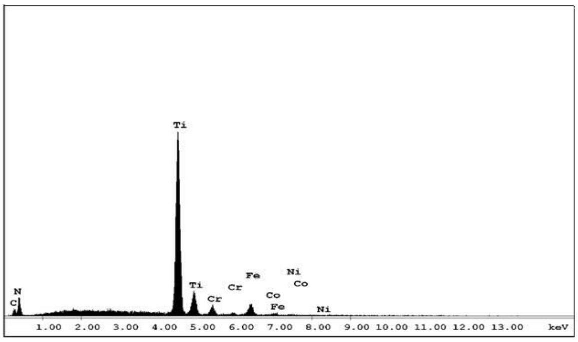

Fig. 2. The elemental composition of the 12X18H10T + Ti coating in the gaseous environment of nitrogen

Table 4

The phase composition of the *12X18H10T + Ti* coating in the nitrogen gas atmosphere

Coating	Phase detection	Phase contents, vol.%
12X18H10T + Ti under nitrogen	$FeN_{0.0324}$	9.8
	TiN	85.5
	Fe-α	4.6

The following properties were identified: nanohardness of the *12X18H10T + Ti* coating in the gas atmosphere of nitrogen (Fig. 3), which is 35.808 GPa; yield modulus of the coating which is equal to 378.56 GPa; flowability is 0.15%; relaxation coating is 0.05 %. To determine all of the above parameters the Poisson's ratio was determined being equal to about 0.27.

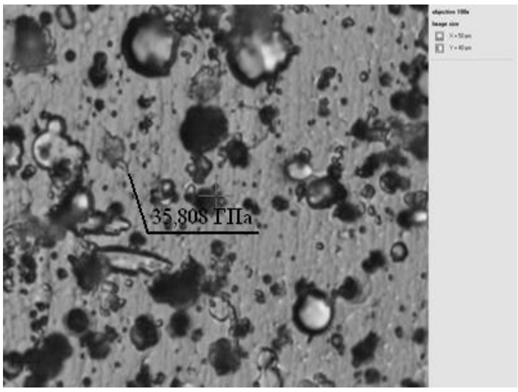

Fig. 3. Nano hardness of 12X18H10T + Ti coating in the nitrogen gas atmosphere

For the coating *Cr–Mn–Si–Cu–Fe–Al* in the nitrogen gas atmosphere, nanohardness is 7.413 GPa.

Table 5 shows the published data on the nanohardness of some materials.

The result of the comparison shows that the hardness of the nano *12X18H10T + Ti* coating in the atmosphere of nitrogen exceeds all the materials shown in Table 5, among which the last three are used as abrasive coatings and reinforcement. The structural and phase analysis revealed that the coating *Cr–Mn–Si–Cu–Fe–Al* in the gaseous environment of nitrogen has two phases $FeN_{0.0324}$ – 60,6 %, *TiN* – 39,4 %, the *12X18H10T + Ti* covering in the gaseous envi-

Table 5

Material properties calculated according to the nanoindentation

Material	H, GPa	E, GPa
Copper	2.1	121
Titan	4.1	130
The multilayer film *Ti*/α–*C:H*	8.0	128
Amorphous ribbon *Zr–Cu–Ti–Ni*	11.5	117
Silicon (100)	11.8	174
Thin film *Ti–Si–N*	28.4	295

ronment of nitrogen has three phases (Table 4). The latter circumstance leads to sharp increase in nnanohardness.

The multi-element coating *Cr–Mn–Si–Cu–Fe–Al* in the nitrogen gas atmosphere possesses nanohardness similar to multilayer film *Ti*/α–*C* : *H*, but it is considerably cheaper than the film.

The basic idea used in this study was as follows: for the generation of multi-streams of ions of various metals deposited on the substrate, we used a multi-phase composite cathode on one gun vacuum unit and single-phase titanium cathode on the other gun. During simultaneous sputtering cathodes of various metal ions in the plasma are mixed, and after deposition, the coating is formed.

Conclusions. The main results of this paper can be summarized as follows:

1. On the basis of a thermodynamic model, the connection between the rate of corrosion and mechanical damage, the surface tension of metal, coatings and their melting point was established.
2. Formulas which are suitable for qualitative analysis and prediction of the rate of destruction and metal coatings in corrosion and deformation were obtained.
3. From the theoretical analysis and the experimental data it follows that to obtain high-quality corrosion-resistant and super hard coatings multicomponent plasma flows should be used.
4. This approach is economically more advantageous than the development of technologies for the production of special steels and steel traditional methods.

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О воспроизводимости однофазного структурного состояния многоэлементной высокоэнтропийной системы Ti–V–Zr–Nb–Hf и высокотвердых нитридов на ее основе при их формировании вакуумно-дуговым методом / О. В. Соболь, А. А. Андреев, В. Ф. Горбань [и др.] // Письма в ЖТФ. – 2012. – Т. 38. – №. 13. – С. 40–47.

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Мета. На основі термодинамічної моделі встановити зв'язок між корозійною стійкістю, міцністю покриттів з їх основними фізичними властивостями. Експериментально дослідити корозійні характеристики та міцності багатоелементних покриттів деталей гірничошахтного устаткування.

Методика. Елементарні носії корозійного, термічного й крихкого руйнування розглядаються як система невзаємодіючих часточок, занурена в термостат. Методами нерівноважної статистичної термодинаміки отримана функція відгуку підсистеми елементарних носіїв руйнування на зовнішнє поле. При нанесенні покриттів використовувалися композиційні катоди, отримані методом індукційного плавлення. Кількісний аналіз елементного складу композиційних катодів проводився на електронному мікроскопі JEOL JSM-5910. Для вимірювання мікротвердості використовувався Мікротвердомір HVS-1000A. Визначення швидкості корозії в різних технологічних середовищах проводилося за ДСТ 9.908-8512. Для визначення корозійної стійкості покриттів використовувався метод анодного поляризаційного ініціювання дефектів (АПІД).

Результати. Розроблено теоретичний підхід до прогнозування властивостей покриттів, нанесених на ці деталі. Теоретичні розрахунки порівнюються з експериментальними дослідженнями. Знайдено зв'язок між швидкістю корозії, поверхневим натягом покриття та температурою плавлення. Отримана формула, що описує деформований стан твердого тіла, включаючи область руйнування. Експериментально визначена корозійна стійкість і характеристики міцності композиційних покриттів деталей гірничошахтного устаткування.

Наукова новизна. Уперше отримано зв'язок між корозійною стійкістю, міцністю покриттів з їх поверхневим натягом і температурою плавлення.

Практична значимість. Отримані формули можуть бути використані для якісного аналізу та прогнозування швидкості руйнування металу й покриття при корозійних, деформаційних і термічних впливах.

Ключові слова: *нерівноважна статистична термодинаміка, функція відгуку, покриття, корозія, руйнування, деформація, міцність, мікротвердість*

Цель. На основе термодинамической модели установить связь между коррозионной стойкостью, прочностью покрытий и их основными физическими свойствами. Экспериментально исследовать коррозионные и прочностные характеристики многоэлементных покрытий на деталях горношахтного оборудования.

Методика. Элементарные носители коррозионного, термического и хрупкого разрушения рассматриваются как система невзаимодействующих частиц, погруженная в термостат. Методами неравновесной статистической термодинамики получена функция отклика подсистемы элементарных носителей разрушения на внешнее поле. При нанесении покрытий использовались композиционные катоды, полученные методом индукционного плавления. Количественный анализ элементного состава композиционных катодов проводился на электронном микроскопе JEOL JSM-5910. Для измерения микротвердости использовался микротвердомер HVS-1000A. Определение скорости коррозии в различных технологических средах проводилось по ГОСТ 9.908-8512. Для определения коррозионной стойкости покрытий использовался метод анодного поляризационного инициирования дефектов (АПИД).

Результаты. Разработан теоретический подход к прогнозированию свойств покрытий, нанесенных на эти детали. Теоретические расчеты сравниваются с экспериментальными исследованиями**.** Получена связь между скоростью коррозии, поверхностным натяжением покрытия и температурой плавления. Получена формула, описывающая деформированное состояние твердого тела, включая область разрушения. Экспериментально определена коррозионная стойкость и прочностные характеристики композиционных покрытий деталей горношахтного оборудования.

Научная новизна. Впервые получена связь между коррозионной стойкостью, прочностью покрытий с их поверхностным натяжением и температурой плавления.

Практическая значимость. Полученные формулы могут быть использованы для качественного анализа и прогнозирования скорости разрушения металла и покрытий при коррозионных, деформационных и термических воздействиях.

Ключевые слова: *неравновесная статистическая термодинамика, функция отклика, покрытие, коррозия, разрушение, деформация, прочность, микротвердость*

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