Досліджені пружні властивості плазмових покриттів ламелярної структури, у тому числі і з нанаскладовими. Визначення модулів пружності здійснювалося методом внутрішнього тертя і випробуваннями на вигин. Представлена методика оцінки балансу енергій в умовах випробувань на вигин, що дозволила розрахувати параметри тріщиностійкості при відшаровуванні і розтріскуванні покриттів. Отримані вирішення для оцінки когезійної міцності, що враховують дисперсність структури і особливості контакту між частками в покритті

Ключові слова: плазмове покриття, модуль пружності, внутрішнє тертя, тріщиностійкість, міцність, багатофазна структура

Исследованы упругие свойства плазменных покрытий ламеллярной структуры, в том числе и с наносоставляющими. Определение модулей упругости осуществлялось методом внутреннего трения и испытаниями на изгиб. Представлена методика оценки баланса энергий в условиях испытаний на изгиб, позволившая рассчитать параметры трещиностойкости при отслоении и растрескивании покрытий. Получены решения для оценки когезионной прочности, учитывающие дисперсность структуры и особенности контакта между частицами в покрытии

Ключевые слова: плазменное покрытие, модуль упругости, внутреннее трение, трещиностойкость, прочность, многофазная структура

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EFFECT OF MULTIPHASE STRUCTURE OF PLASMA COATINGS ON THEIR ELASTIC AND STRENGTH PROPERTIES

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1. Introduction

Coatings, obtained by using the method of metallic plasma spray, are characterized by heterogeneous structure, formed from disk-shaped deformed particles (splats), which are characterized by specific sizes and certain degree of connectedness between themselves. The technology of obtaining such a plasma coating implies the formation of defects in it, including dislocations, microcracks, pores [1–3].

The existence of different types of cracks – vertical, horizontal, those that occur on the body of grain – particle, along the boundary between flattened particles or along the interface between the coating and the base, substantially complicate both theoretical analysis of the processes of destruction and the results of experimental measurements.

Under conditions of loading a composite material (CM) in the form of the system "matrix-coating", the nature of crack formation differs significantly from the analogous processes of origin and propagation of cracks that occur in a continuous solid body. Local states in the area of apex of a possible crack determine coefficient of intensity of stresses and may contribute to or resist the propagation of cracks in the coating itself or in the interphase zone of contact of a solid body surface and a coating. Due to heterogeneity, anisotropy, polyphase structure of plasma coatings, there appear difficulties in selecting methods of studies and further analysis of possibilities of obtaining high physical and mechanical characteristics of the formed coating [4, 5].

In the process of research into mechanical and physical properties, as well as for predicting possible type of destruction of a composition system, it is important, first of all, to analyze elastic characteristics of plasma coatings. Relevant are also the questions, connected with the examination of interrelation of combination of properties of the composite material, obtained in the process of plasma spraying. This relates, first of all, to adhesive and cohesive properties of coatings, physics and mechanics of their destruction, fracture toughness, which, in turn, depend on elastic characteristics and peculiarities of the laminar disc-shaped structure of coatings. Elastic, adhesive-cohesive and strength properties are the most important parameters of coatings and the system "base-coating" as a whole.

2. Literature review and problem statement

A rather large number of studies were carried out regarding physical and mechanical properties, namely, elastic and strength characteristics of plasma (gas thermal) coatings. Nevertheless, as our experience shows, at present there is a lack of substantiated studies, experimental tests and data bases on the properties of coatings for conducting calculations and simulation of the processes to form coatings [1, 4–8].

The papers are known that present technique and analysis of results of the experimental studies, as well as solutions for determining the module of elasticity and strength characteristics when testing the samples with coating for microindentation [6–9], at uniaxial tension [4, 10, 11], for the 3- and 4-point bend [12–14].

At present, for determining elastic properties of coatings, the most common are the standard methods for testing by microindentation [6–9], and the most popular one in terms of sensitivity to the depth of penetration is the method of nanoindentation, in particular using the Berkovich indenter [8]. In the process of microindentation, they record the diagram of introduction of the indenter in coordinates (load P – convergence of h of the indenter and the sample). The method is based on the analysis of initial stage of the curve of load, when deformation has pure elastic character and is subject to the Hertz ratio. For the spherical indenter of radius R, initial expression for the load takes the form:

$$P = \frac{4}{3} E^* R^{0,5} h^{1,5}, \quad (1)$$

where $E^*=E_c \cdot E_i \cdot [E_i\ (1-\upsilon_c^2)+E_c \cdot (1-\upsilon_c^2)]^{-1}$ is the reduced Young's modulus; ν is the Poisson ratio, indices c and i relate to the examined material (coating) and the material of indenter, respectively.

After constructing the obtained data in dual logarithmic coordinates or the $P=f \cdot h^{3/2}$ coordinates, it is possible to determine, first, E^*, and then E of the examined material, including the coating.

Nevertheless, determining characteristics of the surface, not homogeneous, layers, in particular, plasma coatings, is not a trivial solution. In the local places obtained data can essentially differ for certain phases. In this case, one must perform approximation, which makes it possible to estimate the total integral characteristic of crack formation [4]. To determine the module of elasticity E_c and the Poisson coefficient μ_c of plasma coatings, the tests are conducted at static uniaxial tension [4, 10, 11]. During stretching the sample, longitudinal deformation of the base ε_{zs} is measured, longitudinal and lateral deformation of the coating ε_{zc}, ε_{xc} in one and the same sample.

However, in the majority of cases, functional plasma coatings contain ceramic components, which leads in many instances to brittle failure of a coating. The surface roughness, existence of micropores and microcracks, poor cohesion between splats in coating contributes to reduction in elastic and strength characteristics of such coatings and composition as a whole. As it follows from analysis of a small number of publications, manufacturing samples for the tensile tests appears rather labor-consuming. Furthermore, in the analysis of the obtained results, the influence of physical-chemical processes of interaction between a coating and a base in the interphase zone is not considered [4]. Nevertheless, the technique is sufficiently verified based on the example of different types of coatings. The results of studies of elastic characteristics and peculiarities of destruction, depending on the defectiveness of structure and geometric parameters of coatings (thickness, length), are represented in a number of papers [10, 15].

More widespread, compared to the tensile tests of composite materials, are bend tests [4, 12–14] whose results make it possible to obtain and analyze data for calculating the module of elasticity in the linear section. The calculation of modulus of elasticity of the flat samples at bending when the curve "deformation-load" is recorded, depending on the applicable load, sample flexure and its geometric dimensions, is performed by formula [13]:

$$E = \frac{L^3}{4H^3B \times 1000} \frac{\Delta P}{\Delta f}, \quad (2)$$

where L is the distance between supports; H, B are the thickness and width of sample; P is the applied force; f is the sample's flexure.

Application of methods for processing results of mechanical static tests for bending and microindentation makes it possible to obtain and analyze not only the elastic characteristics of coating, but to examine the processes of its destruction in the form of exfoliation or cracking. Based on the results of these experiments, the data were received on crack resistance (fracture toughness), adhesive and cohesive strength of coatings [7, 9, 12–14]. In particular, the method of indentation is one of the most widespread methods, which makes it possible to run both qualitative and quantitative analysis of destruction of compositions of the type base-coating and to determine parameters of crack resistance (K_c). Using the Vickers pyramid, the formation of several possible systems (morphologies) of cracks is examined: cracks under the apex of indenter and in the angles of its imprint. According to the Palmqvist crack system, critical coefficient of crack resistance is calculated by equation [7, 9]:

$$K_C = k \frac{P}{a \cdot l^{1/2}}, \quad (3)$$

where k is the coefficient that depends on the geometry of indenter and the examined material; a is the half of the length of diagonal of the imprint of Vickers indenter; l is the length of crack.

When exploring bending, different sections of the curve of deformation are examined, by which the intensity of released energy is calculated or coefficient of intensity of stresses, as well as analysis of adhesive-cohesive strength of the coatings is conducted [12, 14, 15]. It follows from these papers that, in spite of existing, sufficiently large, collection of semi-empirical dependencies for determining parameters of the coatings, there are the differences observed in their values because of difficulty in consideration of mechanisms of deformation and destruction in each particular case. Nevertheless, obtained data are used as the estimated characteristics for the defectiveness of coatings.

One of the most precise methods of determining normal Young's modulus of elasticity E (shear modulus G) is a physical method of studies, based on measurements of attenuation of energy of elastic vibrations in the volume of a solid body – the method of internal friction (IF). Classical case is the expression, which establishes interrelation between the Young's modulus of elasticity and the resonance frequency (f^2) of fluctuations of the sample, according to dependency $G=K \cdot f^2$, where coefficient K is the function of geometric dimensions and mass of the sample, and in the case of torsional oscillations, when using wire samples, it depends on the moment of inertia of the torsion pendulum [5]. This approach is used for different materials, including composites.

However, for determining elastic properties of particular coatings on the samples, this approach is not correct. For specific regimes (deformation, stress, temperature) of the samples without coating and with coatings based on the experimental data on parameters of internal friction Q^{-1}, it is possible to obtain expression for the modulus of elasticity, as well as coefficient of internal friction of the particular coating Q_c^{-1}, depending on other characteristics of components of the system "base-coating" [5, 16].

In a general case, it is possible to state that standardized or proposed new techniques, as a rule, lead to different results because of particular peculiarities when determining the necessary characteristics in each specific case. Therefore, of interest is comparative analysis of existing data, accumulation of new data and generalization of obtained data, which would consider these peculiarities of plasma spraying.

3. Aim and tasks of the study

The purpose of the work was the analysis, using different calculation-experimental methods of research, of elastic and strength properties of the composite materials, connected with peculiarities of forming the structure and composition of coatings at plasma spraying.

To accomplish the set goal, the following tasks were solved:

– to develop calculation-experimental technique of determining the modulus of elasticity of plasma coatings with the use of measurements of attenuation of elastic vibrations energy (the method of internal friction – IF) and of bending tests;

– to compare the obtained results with the data of other alternative methods of measurements, such as microindentation, tensile test;

– to analyze crack resistance and cohesive strength of plasma coatings taking into account the phase composition and peculiarities of structure of the obtained coatings, as well as the interphase zone.

4. Materials and methods of research into the influence of structure of plasma coatings on the properties of composition

4. 1. Materials and the utilized research equipment

For the research we used Armco-iron and steel with coatings from the sprayed powder materials – Mo, NiAl, NiCrBSi (PG-10) and compositions from the mixtures, which include nano components in the form of oxides SiO_2 (aerosil), $Al_2O_3 \cdot SiO_2$ (alumo-aerosil, symbol – AlaL [5, 17–19].

The coatings were applied to the surface of the samples by plasma spraying at the modernized installation UPNS-304 (made in Ukraine) with the plasmatron, which provided for the laminar discharge of plasma flow.

Physical and mechanical properties of both the coating and the composition "base-coating" were determined by the results of mechanical bending tests, according to the designed calculation-experimental techniques [5, 14, 20]. In particular, the experiments were conducted at the installation of the model KOGEL (made in Germany) whose mechanical part was complemented by a personal computer with installed specific software. The connection between the computer and sensors of the installation was provided by an electronic init in the form of ATsP ADC121S021.

The tests were carried out on the samples of size 100×10×1 with the plasma coatings of thickness 50–150 μm, applied to one side of the sample.

The measurements of energy absorption of elastic vibrations by the method of internal friction for determining the modulus of elasticity of coating were conducted at the installation, which is a "reverse torsion pendulum", fabricated at Physics Department of the T. Shevchenko Kiev National University (Ukraine, Kiev) 5, 19. The measurements were conducted on the wire samples made of pure iron of diameter 1 mm and length 100 mm.

4. 2. Calculation-experimental technique of determining physical and mechanical characteristics of plasma coatings at bending tests

During exploration of physical and mechanical characteristics in the process of bending tests of the material with the coating using the analog-to-digital converter, we recorded the curve "load – deformation", where there are different section-zones observed, corresponding to the given test, which characterize stages of the deformation [5–7, 13, 14]. Calculation of the modulus of elasticity is performed in the first section (at the initial stage), where a linear dependency of stress on elastic deformation of the sample is observed and on its geometric dimensions [5, 13, 14, 20].

The final solution for determining modulus of elasticity of the coating using (2), taking into account flexures of the base and the coating, moment of inertia and after appropriate transformations, will take the form:

$$E_c = \frac{-A + \sqrt{A^2 + C}}{2R^3} E_b. \quad (4)$$

In equation (4), $R=h/H$; $A=4R^2+6R+4-F$; $C=4R^2(F-1)$; $F=f_b/f_{com}=(1+R)^3 \cdot E_{com}/E_b$ are the ratios of flexures of the base to flexure of the composition "base – coating"; h is the thickness of coating; E_b, E_c, E_{com} is the modulus of elasticity of base, coating and the composite "base – coating".

For determining the modulus of elasticity of the composite plasma coating we used the technique, based on measurement of internal friction Q^{-1} of the samples without the coating and with the coating. After processing experimental data of the temperature and amplitude dependencies of internal friction $Q^{-1}=f(T, \gamma)$ (TDIF, ADIF) of the system "base – coating" at the appropriate level of deformations and a specific temperature, parameters of the coatings are calculated, in particular, normal module of elasticity E or shear modulus G [5, 16, 21].

To determine capacity of the material of the coating to resist destruction, the analytical solutions were used, as well as results of the bending experiments, which make it possible to analyze crack resistance of interphase zone of the system "coating – base" and corresponding area of the coating itself at its exfoliation and cracking [5, 20, 22].

The calculation-experimental technique, with underlying positions of classical theory of strength and the results of bending tests, was used for the calculations of cohesive strength of the coatings themselves. As follows from experimental results, at reaching a certain level of load, the origin and growth of specific forms of cracks are observed. Strength in this case is calculated by critical load and at maximum stress in coating, necessary for crack formation in the appropriate sections [5, 12–14]. The final solution for evaluating the strength of materials with coatings at a three-point bending test takes the form:

$$\sigma_{st} = \frac{P_{st} \cdot l}{4} \frac{(e-h) \cdot E_{com}}{J_b E_b + J_c E_c}, \quad (5)$$

where P_s is the load, which causes either cracking or exfoliation of coating, is determined by the diagram; l is the distance between supports; h, H is the thickness of coating and base; $E_c \cdot E_b$ is the modulus of elasticity of coating and base, $J_b \cdot J_c$ are the moments of inertia of base and coating; e is the distance of neutral line from the surface of base.

By using the approaches examined above, we obtain values of critical stresses for appropriate conditions, at which a coating is either destroyed or exfoliated. The given positions are verified based on the example of different types of the systems "base – coating".

5. Results of research into elastic and strength properties of the plasma coatings

5. 1. Determining the modulus of elasticity of composite coating by the method of internal friction

When determining characteristics of plasma coatings by the method of internal friction (IF), the measurements of the temperature and amplitude dependencies of internal friction (TDIF, ADIF) are conducted; in this case, the peculiarities of analysis and processing of results appear in comparison with pure metals.

Examination of the loss factor $Q^{-1}=f(T, \gamma)$, as a function of the modules of elasticity of materials of coating and base, as well as thickness of coating and base, is the subject of paper [16]. Using this method, after a number of transformations, expression for the modulus of elasticity of plasma coating as a function of the modulus of elasticity of materials of the base E_b E_0, thickness of the coating h_c and the base h_b, as well as loss factors (Q^{-1}) for the system "base – coating" takes the form [5]:

$$E_c = E_b h\left(1-\bar{h}\right)^{-1}\sqrt{\left[1+\left(Q_b^{-1}\right)^2\right]\cdot\left[1+\left(Q_c^{-1}\right)^2\right]^{-1}} \times$$
$$\times\left(Q_c^{-1}-Q^{-1}\right)\cdot\left(Q^{-1}-Q_b^{-1}\right)^{-1}, \qquad (6)$$

where Q_b^{-1}, Q_c^{-1} is the internal friction in a base without the coating and in the coating; $\bar{h}=h_c/h_b$ is the relative thickness of coating.

Equation (6) includes a number of components, which are determined for specific modes (deformation, stress, and temperature) directly in the experiment (Q^{-1}, Q_b^{-1}) or are calculated (Q_c^{-1}).

To determine coefficients of internal friction directly in the coating Q_c^{-1} in equation (6), it is possible to use the Favstov solution for describing decrement of elastic vibrations energy attenuation in the system "base-coating" δ_{sys} in torsion depending on a number of parameters [21]:

$$\delta_{sys} = \delta_b + \frac{\bar{G}\left(\delta_c-\delta_b\right)\left(R^4-R_b^4\right)}{\bar{G}\left(R^4-R_b^4\right)+R_b^4}, \qquad (7)$$

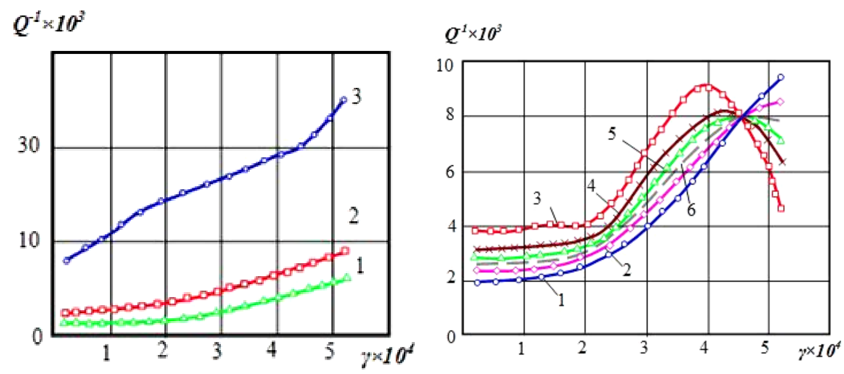
where δ_s, δ_c is the decrement of vibrations attenuation in the base and the coating; $\bar{G}$ is the relative shear modulus; R and R_b is the radius of cylindrical sample with the coating and without the coating, respectively.

By solving jointly system (7), (8) with regard to the fact that the coefficient $Q_c^{-1}=\delta_c/\pi$, we obtain expression for coefficient of internal friction of the coating itself depending on parameters of the system. Fig. 1 demonstrates as an example data on measurements of internal friction (Q^{-1}) in the samples of iron (curve 1) and the system "iron – coating" (curve 2), as well as results of processing these measurements directly for the coatings (curve 3) of Mo and NiAl.

The estimated curves (4)–(7) in Fig. 1, *b* characterize energy losses in the coatings with different possible ratios of the modules of elasticity of coating and base $\bar{E}=E_c/E_b$. Processing these data for the NiAl coating leads to linear dependency of energy dissipation (energy attenuation) of elastic vibrations and ratio of the moduli of elasticity $\bar{E}$ in the form:

$$Q_c^{-1} = 1{,}4\cdot 10^{-2} - 4\cdot 10^{-3}\cdot \bar{E}. \qquad (8)$$

Further combination (6)–(8) makes it possible to determine coefficient of internal friction and modulus of elasticity of the corresponding coating for specific conditions of measurements.



a *b*

Fig. 1. Internal friction in the samples made of iron without coatings (curve 1), samples with coatings (curve 2) and the coatings separately (curve 3): *a* — Mo; *b* — NiAl; curves (4)—(7) are calculated for $\bar{E}$=0,5; 0,8; 1,0; 1,5, respectively

The values of modules of elasticity of the plasma coatings according to the results of measurements and calculations of internal friction are represented in Table 1.

Table 1

Values of Young modules of elasticity and cohesive strength of plasma coatings

Coating composition	Methods for determining modulus of elasticity of coating E, GPa			Strength, MPa	
	IF (equation (6))	Bend (equation (4))	Tension, indentation	σ_{coh}, (equation (14))	σ_{st}, (equation (5))
Mo	100	89, (100 [7])	(65), ((210–290) [7])	71	136
NiAl	99, 28–105	80	131–150	236	284
Al_2O_3	54, (64 [16])	45	82	46	20...80
GP–12 ,10 (NiCrBSi)	111	55	(120 [16])	82	154
AlNi – (SiO_2 Al_2O_3)	157	131–143	119	438	374
GP–10 – (SiO_2 Al_2O_3)	193	86 – 110	185	536	472

Note: in the brackets are literature data, represented for comparison

Table 1 also displays generalized results for modulus of elasticity of the coatings, obtained with at bending tests, according to calculation-experimental technique (4), as well as in tension and indentation. Literature data are represented in brackets. As we see, there are certain discrepancies, sometimes essential.

5. 2. Crack resistance of plasma coatings

5. 2. 1. Energy balance in the system "base – coating" at cracking and exfoliation of the coating

Crack resistance , as well as other physical and mechanical properties, depend on the obtained laminar (lamellar) structure of plasma coatings and are determined by the atomic-molecular bonds between the lamellae in the coating itself and in the interphase zone "coating-base" [3, 5, 13, 17, 20, 22].

The process of crack formation at deformation is characterized by intensity of the released energy G_{1c} in separate local sections of the composition system "base – coating" and, accordingly, by the coefficient of crack resistance K_{1C}. The estimation of energy balance at the moment of crack initiation is assumed as the base of analytical studies. Under the action of load, the coatings of different composition display different forms of destruction – adhesive or cohesive. In practice, the process is realized frequently, during which cracking of the coating is accompanied by its simultaneous exfoliation. In this case, intensity of the entire released energy G is spent both on the cracking and exfoliation of the coating in a certain proportion depending on the properties of coatings and of the obtained composite material. The critical level of released energy depends on the critical load of destruction.

A change in the total elastic energy in the system base – coating, released both at cracking and at exfoliation of the coating, is represented in the form [20, 22]:

$$\Delta U = 2G_b \cdot c + G_c \cdot h. \tag{9}$$

In this case, energies in the base and in the coating are represented as $G_b=(K_{1c}{}^b)^2/E_b$ and $G_c=(K_{1c}{}^c)^2/E_c$, respectively; intensity of the released energy of the system at cracking, equal to the ratio of energy ΔU, spent for this process, to thickness of the coating ($G=\Delta U/h$), takes the form:

$$G = \frac{2G_b \cdot c}{h} + G_c, \tag{10}$$

where c is the half of length of an interphase crack.

Intensity of the released energy of the system at cracking in our case, according to results of the studies, is described by dependency [20, 22]:

$$G = \frac{\sigma_c^2 h}{E_c}\left[\frac{\sigma_c}{3\tau} + \pi f\left(\bar{E}_{cb}\right)\right]. \tag{11}$$

In (11), σ_c is the stress in the coating (applied and residual); $f(\bar{E}_{cb})$ is the tabulated function, dependent on the ratio of modulus of elasticity of the coating and the base $\bar{E}_{cb}=E_c/E_b$; h is the thickness of the coating.

For evaluating the tendency of the system for cracking, they apply the so-called critical parameter of cracking Ψ_c, dependent on the stress in the coating σ and the crack resistance coefficient K_C [20, 22]:

$$\Psi_c = K_c / \sigma\sqrt{h} = \sqrt{\pi f\left(\bar{E}_{cb}\right)}. \tag{12}$$

In the final analysis, the joint solution (10)–(12) leads to expression for the critical number of cracking of the system in the form:

$$\psi_c = \sqrt{\pi f(\bar{E}_{cb}) + 2\int_0^{c/h} \frac{E_c G_1{}^{inph}}{\sigma^2 h} d(c/h) - \frac{2E_c G^{inph}}{\sigma^2 h}\left(\frac{c}{h}\right)}. \tag{13}$$

Formula (13) describes different processes during destruction of the system "base – coating" from the point of view of energy balance, released as a result of cracking and exfoliation of the coating. The first term under the root characterizes crack resistance of the coating itself during development of crack in it, the second one – state of exfoliation of the coating, and the third one describes deformation processes that occur when these two processes take place – cracking/exfoliation.

Fig. 2 demonstrates dependency of the parameter of cracking on the coefficient of crack resistance of the examined compositions. The bold lines indicate the sections that correspond to critical parameters of crack resistance of the examined systems of coatings.

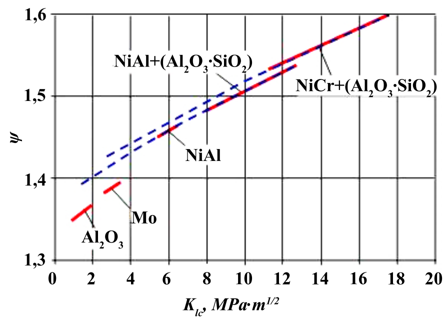


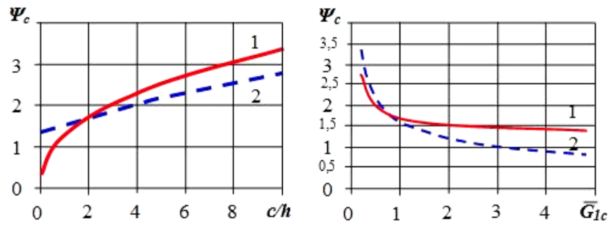
Fig. 2. Theoretical dependency (interrelation) of the criterion of cracking Ψ_c and coefficient of the crack resistance K_{1c} of the coatings

The process of transition from cracking to exfoliation is presented in Fig. 3 in the form of dependencies of the critical parameter of cracking Ψ_c on the ratios of half of length of an interphase crack and thickness of the coating (c/h), as well as ratios of the released energies in the coating and the interphase zone at critical conditions of deformation $\bar{G}_{1c}=G_{1c}{}^c/G_{1c}{}^{inph}$.

Dependency, demonstrated in Fig. 3, *a*, demonstrates that when the condition c/h>2 is met, simultaneous processes of cracking and exfoliation pass into the process of exfoliation; the process of cracking prevails before it. Fig. 3, *b* displays dependency of the critical number of cracking and exfoliation on the ratio of released energy in the coating to the released energy in the interphase zone. It follows from the illustrated results that at the condition $\bar{G}_{1c}=G_{1c}{}^c/G_{1c}{}^{inph}\geq 1$, there occur processes, analogous to the processes, examined above.

Fig. 4 displays theoretical values of the freed interphase energy ΔG (on the border between the base and the particle) in the case of exfoliation of the coating depending on the relative area of physical-chemical contact $\bar{f}_{ph}$ for the NiAl coating.

The influence of the size of original particles of the powder material R_p and the ratio of modules of elasticity of the coating and the base $\bar{E}$ on the dependency $\Delta G \approx \bar{f}_{ph}$. According to results, for the larger particle sizes and at equality of modules of elasticity of the coating/base, the smallest amount of energy is necessary for propagation of an interphase crack. The obtained values are correlated with diameter of particles of the powder, the quantity of interparticle contacts and depend on chemical, phase composition of the coating and on porosity of the coating. Depending on the magnitude of relative contact area $\bar{f}_{ph}$ for appropriate technologies of applying coatings, there is a connection between interphase strength and the parameters of spraying, structure (porosity) and deformation properties (critical deformation) of the coatings [17, 23]. In this connection, fundamental is the fact of the presence of nanocomponents in the material of coating.



a *b*

Fig. 3. Dependencies of the critical parameter of cracking Ψ_c on: *a* – the relative length of exfoliation (c/h); *b* – the ratios of the freed energies in the coating and in the interphase zone $\bar{G}_{1c} = G_{1c}^{c} / G_{1c}^{inph}$, (c is the half the length of an interphase crack, h is the thickness of coating). Curve 1 describes exfoliation, curve 2 – cracking

The values of coefficients of the intensity of stresses K_{1c}, which correspond to the values of intensity of the released energy at exfoliation or cracking of the coating G_C, are given in Table 2.

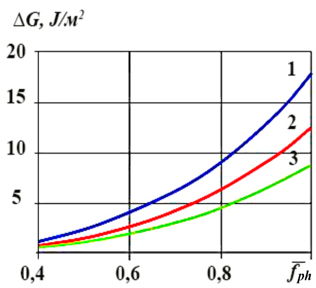


Fig. 4. Calculated dependency of intensity of released energy during development of interphase crack on the relative area of a single contact of particles of NiAl of the coating for different ratios of modules of elasticity of the system coating/base and at different values of radius of particles of the original powder: 1 – $\bar{E}$=0,25, R_p=25 μm; 2 – $\bar{E}$=0,5, R_p=35 μm; 3 – $\bar{E}$=1, R_p – 50 μm

5. 2. 2. General analysis of the process of crack formation at static tests

The obtained results correspond to the critical values of intensity of energy and coefficient of crack resistance for the examined systems, which characterize cohesive and adhesive strength for each particular zone separately, as well as integral indices K_{1C}, ΔG_{Σ} for the system as a whole. These data, obtained based on theoretical examination of energy balance during crack formation in the coating, are presented in Table 2. According to the results of widespread methods of evaluating the crack resistance K_C of the coatings, based on results of bending tests, tension tests, indentation (nanoindentation), the cracks are revealed in the coating, which are spread perpendicularly and in parallel to the interface surface, as well as by the interphase zone. At different methods of testing, examination of coefficients of crack resistance K_C for different sections of the system provides the possibility to determine the character of its cracking.

Table 2 displays in brackets the results of such alternative studies on crack resistance of plasma coatings, as well as numerous literature data. It is necessary to note that crack resistance is controlled by connections between lamellae in the coating. Determining the beginning of propagation of a crack on the curve "load – flexure" is hindered because of characteristic laminar composition structure of coating, its defectiveness, and this is the main reason for the difference in data on crack resistance, which follows from Table 2.

Theoretical estimation of crack formation, based on energy balance in the system, does not imply separate examination of cracks in different directions with respect to the interface boundary (perpendicular or parallel).

Table 2

Crack resistance K^{1c} (MPa·m$^{1/2}$) of plasma coatings and the system "base – coating"

Coating composition	Systems (general)	Coatings (local, cracking)	Interphase zone (exfoliation)	Coatings (experiment)
Mo	3,32	3,198	1,09	(0,93...3,2 [7])
NiAl	6,44	6,04	2,74	1,6
Al_2O_3	1,2	(1,8 [3])	0,47	(1,84 [3])
NiCrBSi	4,5	3,7–5,5	1,8	1,84
NiAl+Alal	12,42	11,1	6,83	6,83–11,0
NiCr+Alal	18,93	16,24	11,928	12,0–16,0

But even with a certain approximation, experimental and calculated values of crack resistance have similar values (Table 2).

These values of crack resistance can be compared to such very important properties as adhesive and cohesive strength of the considered coatings [5, 20, 22].

5. 3. Cohesive strength of plasma coatings

The magnitude of cohesive strength of the coating is affected by a number of factors. Such factors, first of all, include ratios of modules of elasticity of the basic material and the second phase, non-equilibrium state of boundaries of different sections inside the composition, boundaries between the deformed particles.

Crack resistance and cohesive destruction are strongly dependent on the bonds between the lamellae.

For theoretical evaluation of the cohesive strength of a plasma coating we will use the approach, applied to a porous body. If we consider plasma coating as a material in the form of dispersed compact body, then the theory of mechanical strength establishes connection of structure of such a composition body depending on radius of the particles R_p, diameter of the pores D, with a quantity of interparticle contacts and with strength of such structure of the body P_m in the form of dependency [24]:

$$P_m = p'/4R_p^2 n^2 = p'/D^2(\alpha/n)^2 = 10^{10} p'(1/D^2)\beta. \qquad (14)$$

The sample may, with a specific approximation, be used for a cermet body of the type of plasma coating.

Ref. (14) represents the parameter p/ by strength of a single area of contact between flattened particles, the number of these single contacts and factor β, which is a function of porosity of the coating, density of the solid phase and volume of pores per unit of mass [24].

To evaluate strength of the single contact area p' in (14), we will use positions of the theory of destruction, when it examines limiting state at the moment of origin and propagation of a microcrack, which leads to destruction of the material, characterized by the appropriate stress coefficient K_{1c}. In our case, a contact zone between the two flattened particles during tensile test can be represented by a model of material, weakened by interphase crack in the coating

[25]. Expression for the load, necessary for destroying such a separate contact area between the particles, takes the form:

$$p' = 2y\sqrt{2y}\cdot K_{1C}\cdot\left(1-f\left(z\right)\right)=$$
$$= 2\cdot y\cdot\sqrt{2\pi\cdot y\cdot(1-\nu^2)^{-1}\cdot \bar{f}_{ph}^{d}\cdot E\cdot\gamma_{inph}}, \quad (15)$$

where y is the radius of the contact area; (z)=0,339z^2+ +0,136z^5, z=2y/x; x is the distance between contact areas; for our conditions, function f(z)<<1.

When constructing dependency (15), they proceeded from the following considerations. Coefficient of stress intensity in equation (3) takes the form $K_{1c}=\sqrt{G_{1c}}\cdot\sqrt{E_c}$ and characterizes crack resistance of the interface between the coating particles. Intensity of the released energy of the system at cracking of coating is expressed in a general case as $G_{1c}=2\gamma_c$ while effective surface energy $\gamma_c=\gamma_{inph}$ relates to the total area of a single area of the contact f_{ph}, flattened in the process of impact of the particle with radius $y=2{,}03\cdot R_p$ [25].

In the process of formation of a multilayer plasma coating, strong bond is realized not over the entire area of physical contact f_{ph} between atoms of the interacting deformed particles, but only on its certain part f_d that consists of specific number of active centers. According to position about dislocation character of active centers, we assume that area of the active center with high energy is determined by stress field of the dislocation, which reached the contact surface, as well as by fields of the adjacent dislocations [26].

At the same time, according to analysis of the processes, caused by the appearance of dislocations onto the surface of the area f_{ph}, the share of the entire complete surface $f_d/f_d=\bar{f}_{ph}^{d}$, which participates in the formation of durable chemical bonds by the mechanism of plastic deformation, will amount to $\bar{f}_{ph}^{d}=\rho\cdot S_d$. The area S_d. is the area of a single active center, on which durable chemical bonds are formed. Dislocation density ρ can be calculated by the results of measurements of internal friction and calculations of dislocation structure – magnitudes of dislocation grid and segments [5, 17–19, 23, 25]. According to available results, dislocation density, depending on the technology of coatings spraying, reached $\rho=(2...5)\cdot10^7$ cm^{-2} at the area of a single active center, accepted for approximate calculations equal to $S_{dmax}=7{,}8\cdot10^{-9}$ cm^2. Then, according to experimental and calculation data, relative contact area, on which durable chemical bonds between the flattened particles are formed, is within the limits $\bar{f}_{ph}^{d}=0{,}1...0{,}6$ depending on the components of plasma coating. Since the area of active centers with durable bonds is examined, then, accordingly, the area of interaction and the value of energy decrease, and in (15) it is necessary to consider that $G_{1c}=2\cdot\bar{f}_{ph}^{d}\ \gamma_c$, that is, cohesive strength, as well as crack resistance, depend strongly on bonds between the lamellae.

The magnitude of relative contact area substantially affects the processes of destruction that occur at loading the materials with coatings, and it is examined in this work relative to parameters of crack resistance.

Fig. 5 presents dependency of the breaking load p' in (14), (15) on the relative area at destruction of a single contact of diameter $d_{con}\approx2\cdot R_p\cdot\bar{f}_{ph}$ between two lamellae. Marks «+» (broken curve) show values of coefficient of crack resistance, related to the interphase zone with a specific diameter of contact of two deformed particles and corresponding destructive force.

The calculated values of general strength, according to solution by (14) and (15) converted per unit area, are represented in Table 1. To calculate strength of a composite porous coating, according to (15), we accept data from Table 2 as the values of intensity of stress for K_{1c}. Table 1 also demonstrates the data obtained on the basis of calculation-experimental technique in accordance with (5). A certain correlation between the calculated values of cohesive strength (14), (15) and breaking stress (5) is observed.

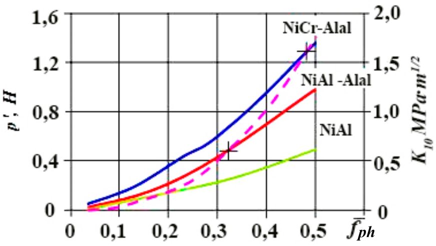


Fig. 5. Dependency of effort, necessary for destroying a single contact area, on the relative contact area of two lamellae from powder: 1 – NiAl; 2 – NiAl – (Al_2O_3–SiO_2); 3 – NiCr – (Al_2O_3–SiO_2)

6. Discussion of results of the effect of structural peculiarities on the module of elasticity, crack resistance and adhesive-cohesive properties of plasma coatings

An important characteristic of the examined coatings is specific microstructure in the form of disc-shaped crystallites (splats), which are in physical-chemical contact among themselves whose level is determined by many factors. For this structure, characteristic are the existence of a complex network of pores and microcracks in the particles body.

As it follows from results of the studies (Tables 1, 2), there is a significant variation in the obtained values of module of elasticity, cohesive strength, crack resistance of plasma multiphase coatings. Essential feature of the obtained results is a strong influence on the modulus of elasticity of micro – structural parameters, such as thickness of the flattened particles, diameter of the contact area and distance between the area of contact in real coatings. Such a non-equilibrium state and complex structure contribute to realization of specific stressed state in the interphase zone and in the coating itself and, therefore, lead to the formation of different dislocation structure in these areas of the system "base – coating". Depending on the composition formulation, conditions of conducting experiment, dynamics of the dislocations at deformation changes and it is possible to obtain different physical and mechanical characteristics of coatings. For example, different data on the modulus of elasticity E_c were received in the case of spraying onto iron and steel (X18H10T). Such results can be explained by using different methods of measurements and analytical processing of experimental data by different authors.

From analysis of the standard curve "stress-strain" during bending tests in the process of deformation in appropriate sections of the coating and in specific moments, they observed, at the particular load P, the origin and further rapid development of crack. Cracks may spread both in the horizontal (parallel to the interface) direction and in the vertical through the basic layer of coating to the interface boundary and may develop subsequently into an interphase crack [5, 7, 12, 20]. Manifestation of one or another system of cracks is connected both with the technology of obtaining coating, in accordance with its structure, chemical and phase composition, and with the magnitude of applied load.

Local states in the area of apex of a crack play the main role in the behavior of crack under loading conditions. The peculiarities of crack formation are the consequence of laminar structure of a plasma coating, which is formed from splats. In this connection, during the application of stresses, temperature fields, destruction (crack formation), first of all, may occur via cracking of the coating itself and/or its exfoliation. Residual stresses that appear in the coating may contribute to the screening of cracks, moreover, excellent in the case if they act perpendicularly to the direction of propagation of cracks or in parallel to the interface boundary of the system "coating – base", according to [7]. Creation of a network of microcracks may cause the screening of apex of the head crack, thus changing the conditions of crack formation. Thus, for example, a low value of modulus of elasticity of the molybdenum coating (65 GPa) compared to steel (210 GPa) leads to significant screening of cracks, caused by elastic mismatch.

Crack formation during indentation, in spite of certain similarity with the bending tests, are characterized by its special features. The values of crack resistance in the parallel or perpendicular directions of indentation are determined by microstructure of the splats and by the accuracy of determining the coefficients k in (3). Differences in the obtained data are connected, in the first place, with the selected zone of action on the sample, and, accordingly, with the selected calculation technique. In this case, boundary between the splats proves to be the weakest component of microstructure of the plasma coating.

For the examined systems "base – coating", the character of fracture of coating under conditions of the applied bending stress is various.

It follows from the results of bending tests of a Mo-coating that the crack resistance for the perpendicular direction is approximately 3 MPa √m, and total crack resistance for the parallel direction of crack propagation is 2 MPa √m.

Adhesive destruction was observed for the Al_2O_3 coating; in this case, intensity of released energy in the interphase zone reached 25–30 J/m^2. For the Al_2O_3 coating, the coefficient of intensity at the modulus of elasticity E_n=82 GPa, amounted to K_{1c}=1,17 MPa √m. This value corresponds to the relative area of physical contact, which is approaching a value of 0,4, which may be considered a limiting value for the transition to exfoliation of coating.

With an increase in the coating density and with its modulus of elasticity approaching elastic characteristics of basic material, the probability of cracking decreases, resistance to destruction increases. Under these conditions, the probability of exfoliation along the interphase zone increases, on one hand, but, on the other hand, destruction of surface layers of the basic material is possible, especially at durable adhesion bonds, when physical contact area approaches the theoretical maximum ($\overline{F}_{ph} \rightarrow 1$) [20]. In this case, the coefficient of crack resistance for aluminum oxide increases up to 3,6 MPa m$^{1/2}$. Changing the technology of spraying, it is possible to change coefficient K_{1C}, since the surface energy of grain boundaries changes due to different factors.

For the coatings based on the thermo-reacting powder NiAl, predominantly cohesion destruction of the coating was observed, in this case, intensity of the released energy in the coating reached the order of 50–65 J/m^2. Coefficient of crack resistance for the coating AlNi in the region c/h~2 was K_{1c}=5,636 MPa·m$^{1/2}$.

A study of the coatings based on the mixture AlNi – SiO_2 revealed that the coatings demonstrate cohesive character of destruction; in this case, intensity of the released energy reached the order of 75–85 J/m^2. The coatings demonstrated rather high indices of the fracture toughness (Tables 1, 2), which is explained by the presence of ultra-dispersed oxide nanocomponent SiO_2 in the powder mixture that possess high reactivity [17], also in the combination with a specific technology of its spraying.

Table 2 vividly demonstrates that, compared to the traditional coatings, materials with ultra-dispersed components have higher (approximately by 2 times) indices of crack resistance, both of the interphase zone and the coating.

The performed calculation and analysis of mechanical tests of the samples with different types of plasma coatings established interrelation between fracture toughness of the coating itself, as well as of the interphase zone, with some microstructural and technological parameters of spraying.

7. Conclusions

As a result of conducted research into internal friction of the system "base – coating", as well as mechanical bending tests, we calculated the modules of elasticity of composite plasma coatings in accordance with the developed technique. Creation of different mechanical mixtures of coatings with presence of ultra-dispersed components (aerosils) leads to the increased elastic properties of composite materials.

In the comparative analysis of elastic properties of plasma coatings with multiphase structures, a considerable variability in the values of modulus of elasticity is observed, which is possible to explain by using different methods of measurements and analytical processing of experimental data by different authors.

The coatings, examined in the work, demonstrated considerably high indices of fracture toughness. These results are explained by the presence of dispersed nanocomponent in the powder mixture in the form of aerosil (SiO_2) at the appropriate technology of plasma spraying. It follows from the obtained data that materials with ultra-dispersed components have higher indices (approximately by 2 times) of crack resistance, both of the coating itself and of the interphase zone.

It is argued in the course of examination of exfoliation or cracking that, due to characteristic laminar composition structure of the coating, its defectiveness, determining the start of crack propagation on the curve "load – flexure" is hindered, and this appears to be the basic reason for the variability of data on crack resistance in the course of comparative analysis with other original sources.

The values of intensity of the released energy G_c and coefficients of intensity of stresses K_c at exfoliation or cracking are compared to such properties as adhesive and cohesive strength of the considered coatings. The presence of nanocomponents in a multiphase coating contributes to the formation of durable cohesive and adhesive bonds inside the coating and along the interphase zone.

Under conditions of multiphase structure of a plasma coating, the character of origin and development of microcracks is predetermined by non-equilibrium state of boundaries between separate flattened particles, by the level of their interaction in the contact zone, by the ratio of modules of elasticity of different crystallites in a coating.

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