Fracture of thin coatings based on multi-component oxides in friction contact

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Abstract. The study of new types of coated materials in different friction conditions is one of the most important trends of tribology. Here we consider thin (up to 300nm) relatively hard nano-structural coatings based on multi-component oxides. The materials are characterized by high resistance to heating and the coatings have almost perfect adhesion to the substrate. The influence of the coatings composition on their mechanical properties and wear resistance is investigated. Micro hardness and elastic characteristics of the coatings are obtained from indentation data. For elastic indentation conical diamond counter-body with rounded tip is used and Young modulus is calculated taken into account the compliance of substrate material. Tribological tests are performed for different coating compositions and different thicknesses both in dry and lubricated conditions. It is obtained that friction coefficient depends on the coating structure, and wear resistance depends also on thickness and the mechanical parameters of the coatings.

Introduction

Carboxylate thermal decomposition methods are usually used to obtain coatings for various purposes, such as: HTSC, ferroelectric, piezoelectric, dielectric, magneto-optic, anti-frictional films [1] and films for special purposes. In JSC "ARRICT" these methods were developed for the formation of uranium oxide layers on fission camber electrodes [2, 3, 4]. Recent research is focused on modification of the technology in order to obtain thin coatings, which can improve the durability of details in friction conditions [5]. The chemical-structural modification technology is characterized by the following features:

- Simplicity and low cost of the technology
- The arbitrary shape of treated surfaces
- The modified layer can be composed from different oxides in various proportions
- The coatings deposition decreases the roughness of treated surface

The study of the coatings includes friction tests, the microscopic analysis of the surfaces before and after the friction tests, determination of elastic properties of the coatings from indentation tests, modeling of friction contact of the coatings. The main purpose of this complex investigation is to determine the main mechanism of the coatings failure and to analyze the influence of the coating thickness and the strength characteristics of coating-substrate interface on the fracture process.

Coatings deposition

The chemical-structural modification process includes the following stages:

- preparation of the modifying composition
- surface preparation (surface degreasing)
- deposition of modifying composition (using brush, spatula or via dip-coating or spray method)
- preliminary heating
- carboxylate thermal decomposition and formation of the coating

Various methods of surface heating can be used. The temperature of preliminary heating is 80-100°C, the temperature of carboxylate decomposition is about 550°C.

The coatings thickness is from 60 to 300 nm for different layer compositions. Steel and quartz glass coated samples are prepared for tribological tests and for indentation tests correspondently.

The results of friction and wear testing

All coatings were tested in similar load and velocity conditions. The scheme of sliding contact is presented at Fig.1. The curvature of the samples is caused by heating-cooling stages of coating deposition, it's minimum value *R* is 0.5m. The samples are made of steel 12X18H10T HRc 40...42 in the form of cylinder with diameter of 6.5 mm and a thickness of 4 mm, on one of the ends of which were the coating.

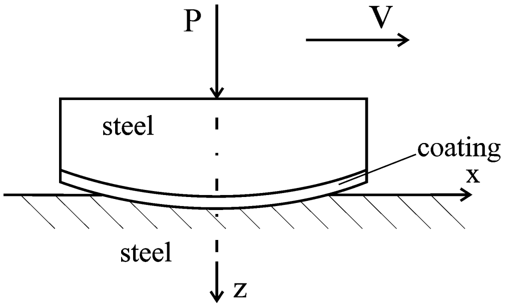


Fig.1. The scheme of sliding contact in friction tests

Universal tribometer UMT-2 (Center for Tribology Inc., USA) is used for friction tests. The test sample is placed in the holder until it stops in a spherical support. The coated surface gets into the contact with the working surface of the counter-body, which is steel disk (HRc 62...65).

All samples are loading by the normal load to the pressure *P*=3.3 N, the rotation frequency provides linear sliding velocity V=0.05 m/sec for the central point of the sample.

A typical dependence of friction coefficient on time for the case of dry friction is presented at Fig.2. At the first stage of the process the friction coefficient is relatively low and stable, but then the friction becomes unstable. It means that we have almost no coating in the contact at this stage; the steel substrate is in contact with the steel counter-body (the particles of the coating material in contact can be treated as abrasive). In order to determine the main mechanism of the coating fracture the contact surface after the experiment is analyzed by the methods of optic microscopy. For this analysis we choose the sample after the shot friction experiment (the half-time of the first stage). The result is presented at Fig.3. White and grey spots at the left and right parts of the surface are steel substrate, and colored sports are the parts of the coating. We have some mix of these types of spots, it should be caused not by wear but by the coating delaminating. Wear is characterized by well-seen boundary between the coating and the substrate.

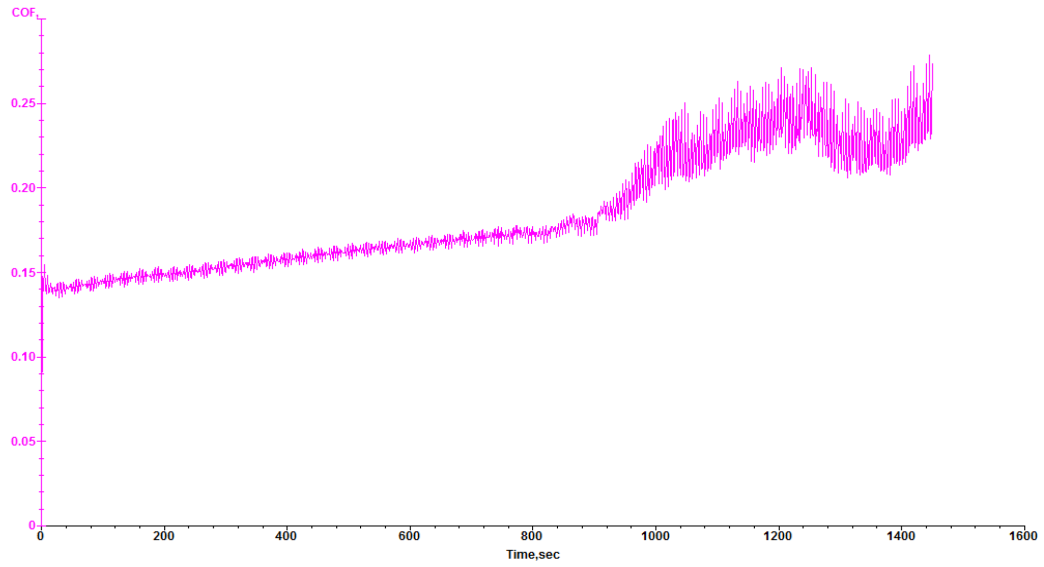


Fig.2. The dependence of friction coefficient on time for Al oxide coating, thickness is 150 nm (dry friction)

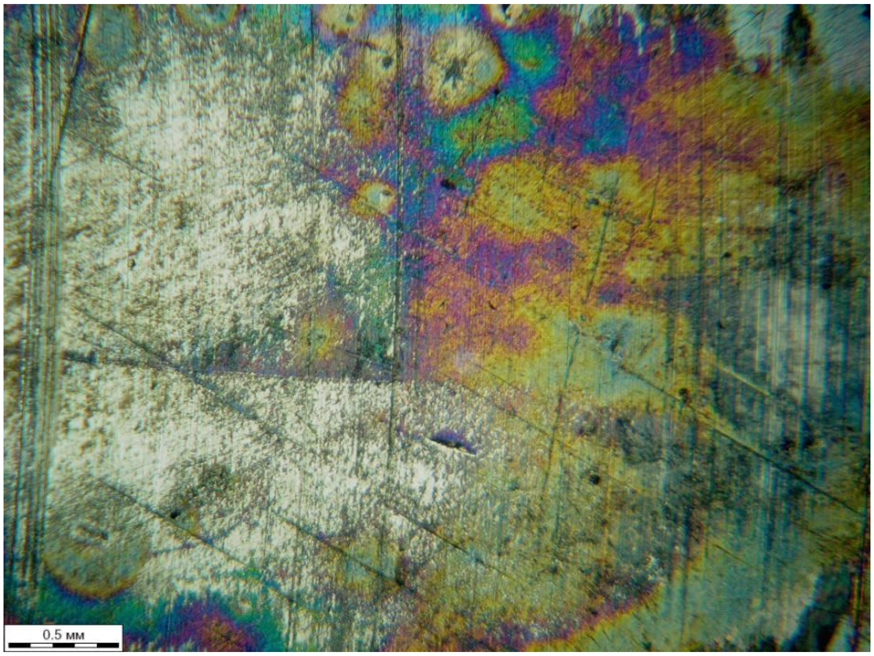


Fig.3. Surface of the coated sample (Al + Cu oxides) after dry friction tests.

Determination of elastic properties of the coatings

Coating delamination is usually initiated at the points of stress concentration. The internal stresses in the coating and the substrate should be calculated for the materials with known Young modulus and Poisson ratio (E_1, ν_1 for the coating and E_2, ν_2 for the substrate). In this study we consider new materials and coatings with nano-thickness. It is a reason to use nano-indentation results to find elastic properties of the materials. Special samples (coated quartz glass) are prepared to provide the surface with small roughness, which is required for reliable indentation results.

NanoTest 600 (MicroMaterialsLtd., UK) is used for nano-indentation tests. Diamond conical indenter is used to provide elastic penetration. The radius of curvature of the indenter tip is 10mkm. The loading and unloading curves are obtained during the tests.

The method of calculation of the coatings elastic properties. The method is based on the contact problem solution for two-layered elastic half-space and smooth axisymmetric indenter. The perfect adhesion between the layer and the substrate is considered:

$$\begin{aligned} & w^{(1)} = w^{(2)}; \quad u^{(1)} = u^{(2)}; \\ & \sigma_z^{(1)} = \sigma_z^{(2)}; \quad \tau_{rz}^{(1)} = \tau_{rz}^{(2)}; \quad \tau_{\theta z}^{(1)} = \tau_{\theta z}^{(2)}, \\ & i = 1..2 \end{aligned} \tag{1}$$

Here w and u are normal and tangential displacements, i =1 for the layer and i =2 for substrate, $\sigma_z^{(i)}$, $\tau_{rz}^{(i)}$, $\tau_{\theta z}^{(i)}$ are stresses. The contact conditions at the upper layer bound are the following:

$$\begin{aligned} & w^{(1)} + w^{(3)} = f(r) + D, && 0 < r < a; \\ & \sigma_z^{(1)} = 0, && a < r < \infty; \\ & \tau_{rz}^{(1)} = 0, \quad \tau_{\theta z}^{(1)} = 0. && \end{aligned} \tag{2}$$

Here $f(r)$ is the shape of the indenter, $w^{(3)}$ is the elastic displacement of the surface of indenter, a is unknown radius of contact zone, D is penetration.

The equilibrium condition is the following:

$$P = \int_0^{2\pi} \int_0^a p(r) r dr d\varphi \tag{3}$$

Contact pressure $p(r)$ is unknown, P is the normal force acted on the indenter.

The method of contact problem solution is presented in [6], it is based on Hankel integral transforms and iteration procedure. The contact pressure is obtained as piece-wise function. For our case it is impossible to solve inverse problem and to find elastic properties of the coating for known values of P and D. Instead of this we can solve the problem (1)-(3) for different values of Young modulus and Poisson ratio from fixed ranges of E_1 and ν_1 and choose the values which provide an experimental value of penetration. It point at force-penetration experimental curve resulted in some values of requested characteristics, but the dispersion is small for high accuracy of measurements and calculations.

Indentation results and analysis. The first step is the determination of the substrate elasticity parameters. The special uncoated quartz glass sample is treated by the conical indenter. The properties of the indenter material are described by NanoTest manufacturer: Young modulus is E_3=1200GPa and Poisson ratio is ν_3= 0.2. The results of ten indentations in different points of the surface are presented at Fig.4. The difference between loading and unloading curves is small enough to conclude that indentation is elastic. This difference is probably caused by the surface roughness. The elastic modulus of uniform material is calculated by NanoTest program based on the Hertz contact problem solution. For our sample the Young modulus is 102GPa (it is greater than the table value 70 GPa).

The results of similar indentation test for coated sample are presented at Fig.5 for ZrO_2 coating. We use average results for calculation of elastic parameters of the coating material. Twenty points on unloading curve are used for calculations (with acting load from 2 to 10 mN). The average values are obtained for each coating. For ZrO_2 coating the calculated Young modulus is 199GPa and Poisson ratio is 0.243. The calculated values for Al_2O_3 coatings are 280GPa and 0.211 for Young modulus and Poisson ratio respectively. The Young modulus for bulk Al_2O_3 material is 370GPa; such difference is probably caused by special structure of ultra-thin layer.

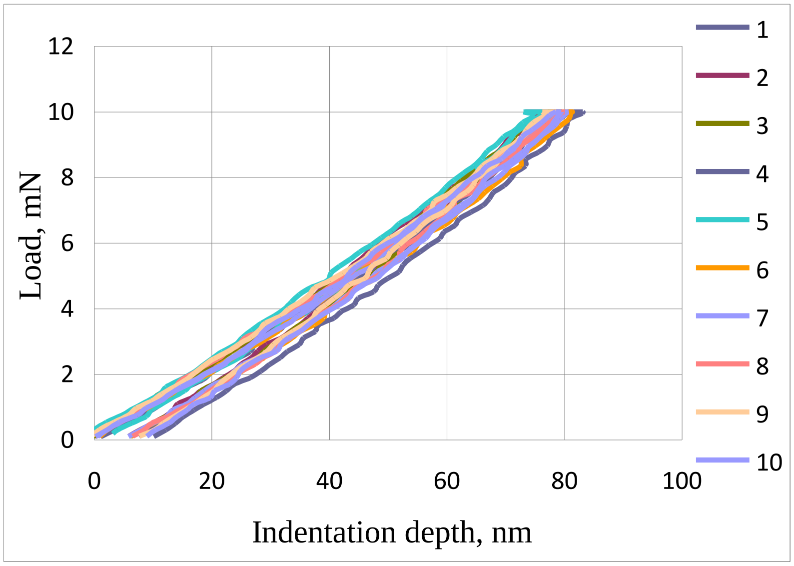


Fig.4 Indentation results for uncoated quarts glass

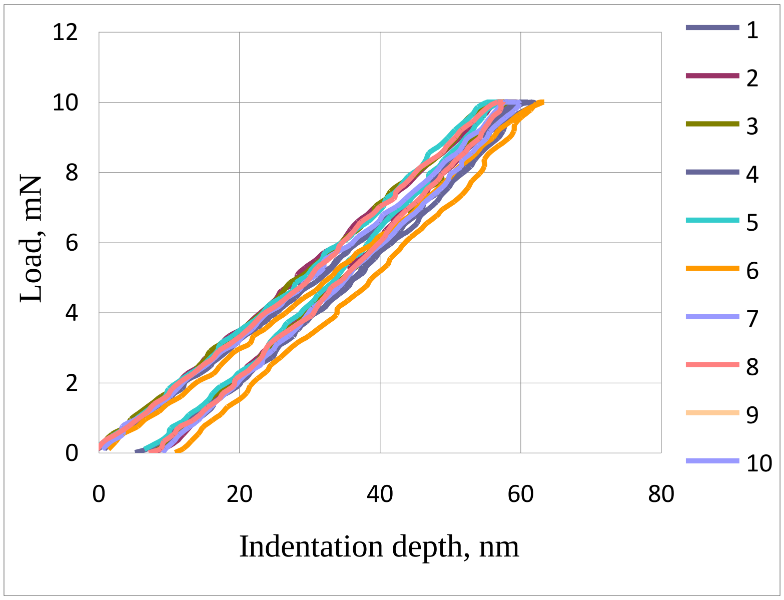


Fig.5 Indentation results for quarts glass coated by ZrO_2

Calculation of internal stresses in coatings.

The geometry of contact presented at Fig.1 and the large curvature of coated sample makes it possible to neglect the influence of thin coatings on contact problem solution. We use Hertz solution of the contact problem for two steel bodies with elasticity modulus 210GPa. The calculated radius of the contact zone *a* is 0.18mm. The curvature of the surface (0.5m) is mach more than the radius of the contact spot, that's why the model of two-layered elastic half-space is used to calculate stresses in coatings and the substrate.

The method of calculation of internal stresses in coated half-space. The assumption that friction does not influence on contact pressure [7] makes it possible to consider the following conditions at the upper layer bound:

$$\begin{array}{lll} \sigma_z(x,y) = -p(x,y), & \tau_{xz}^{(1)} = -\mu p(x,y), & (x,y) \in \Omega; \\ \sigma_z^{(1)} = 0, & \tau_{xz}^{(1)} = 0, & (x,y) \notin \Omega; \\ \tau_{yz}^{(1)} = 0, & & \end{array} \qquad (4)$$

where *p(x,y)* is the contact pressure, and μ is the friction coefficient.

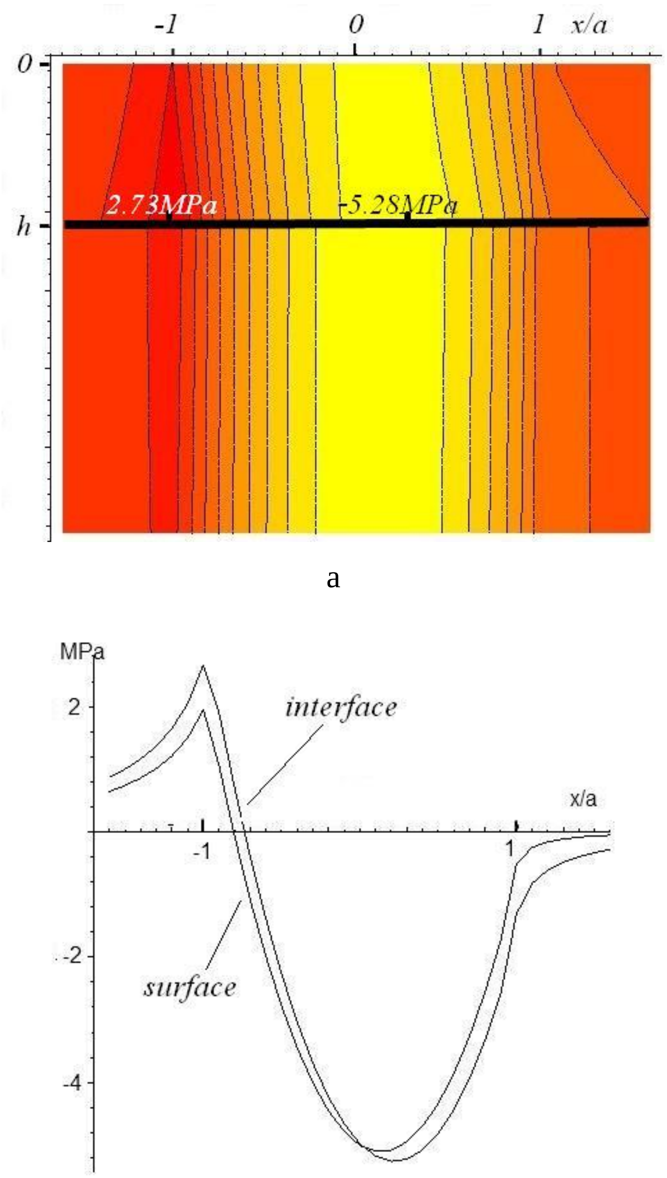
Three-dimensional problem (1), (4) is considered to obtain stresses inside the coating and the substrate. Boundary element method is used to solve the problem. The contact area is divided into squares with constant pressure in each of them. With subdivision *m*, boundary condition (4) develops into the following:

$$\begin{array}{lll} \sigma_z^{(1)} = -\gamma_j^k p_0, & -a + \frac{a}{m}(j-1) < x < -a + \frac{a}{m} j, & -a + \frac{a}{m}(k-1) < y < -a + \frac{a}{m} k; \\ \sigma_z^{(1)} = 0, \quad \tau_{xz}^{(1)} = 0, & a < r < \infty; & \\ \tau_{xz}^{(1)} = -\mu \gamma_j^k p_0, & -a + \frac{a}{m}(j-1) < x < -a + \frac{a}{m} j, & -a + \frac{a}{m}(k-1) < y < -a + \frac{a}{m} k; \\ \tau_{yz}^{(1)} = 0, & 0 < r < \infty. & \end{array} \qquad (5)$$

Here p_0 is the maximum contact pressure; non-dimensional coefficient γ_i^k, which determines pressure in each square, is obtained from solution of contact problem, $0 \le \gamma_i^k \le 1$.

The internal stresses in two-layered elastic body can be obtained by superposition. The method based on double Fourier transforms has been developed to calculate the internal stresses [8].

The results of stress calculation. Here the results are presented for an alumina coating, which thickness is *h*=230nm. The friction coefficient μ is 0.15 (this value corresponds to the first stage in friction test, see Fig.2). The results of friction test and surface analysis are typical for brittle type of coating fracture. It is the reason to study tensile-compressive stresses inside the coating. The stresses are presented at Fig.6. The concentration of tensile (positive) stresses at the surface and at the coating-substrate interface and the formation of the large zone of tension over the coating leads to the its fracture in friction conditions.



a

b

Fig.6. Distribution of tensile-compressive stresses inside the coating and the substrate (a), and at the surface and at the coating-substrate interface (b). The cross-section is in sliding direction and through the center of the contact circle.

Conclusions.

The complex analysis of friction contact of bodies coated by oxides layers and of the fracture of these coatings due to friction is presented in this study. It includes friction tests, indentation tests, calculation of internal stresses in friction contact. The method of determination of elastic characteristics of the coating from the indentation tests is developed and used for oxide coatings.

The results of friction tests, microscopic study of surface after friction and stress analysis makes it possible to conclude that these relatively hard coatings are brittle. The friction coefficient in dry contact with steel is relatively low, but contact stresses should be decreased to avoid fracture in friction contact.

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