THE ANALYSIS OF Al_2O_3 COATINGS OBTAINED BY MAGNETRON SPUTTERING

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ABSTRACT

With the use of AFM, nanohardness and elastic modulus measuring, as well as measurements of the forces of cohesion, friction coefficient by means of a scratch test, oxide coatings of Al_2O_3, obtained by magnetron sputtering of Al were investigated.

The hardness of the coating Al_2O_3, nanostructured film deposited on TiN, increased as compared with the coating deposited on steel. A comparison of the morphology of samples obtained by reactive magnetron sputtering synthesis and a source of RF plasma using oxygen ions was carried out. The mechanical characteristics of hardness, elastic modulus, adhesion strength and friction coefficient of obtained coatings were investigated.

Key words: Aluminium oxide, adhesion, magnetron sputtering, roughness, hardness, friction coefficient.

INTRODUCTION

Aluminum oxide films Al_2O_3 are among the most promising materials. Their exclusive range of mechanical and physical properties (high hardness, excellent corrosion resistance, high stiffness, excellent thermal conductivity, high electrical resistivity, good wear resistance, chemical inertness, etc.) makes it indispensable in the manufacture of Al_2O_3 corrosion, wear and heat resistant products for a variety of industries [1].

Among the huge number of physical methods of deposition of oxide films are the following: Thermal evaporation of metals and semiconductors in a vacuum. Oxides tend to have high melting points, which limits the wide application of this simple and effective method. However, for some oxide systems use thermal evaporation is possible and it is widely used to produce films of V_2O_5.

Reactive magnetron deposition – one of the most common ways to obtain oxide films [2]. Usually there are used different forms of DC (direct current) or RF (radio frequency) magnetron sputtering of metal targets, or RF sputtering targets of massive oxide plasma with various ratios of Al and O_2. By changing the composition of the target, substrate temperature, the gas mixture and dis-

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charge power oxides both the highest and lowest oxidation state of the family can be obtained.

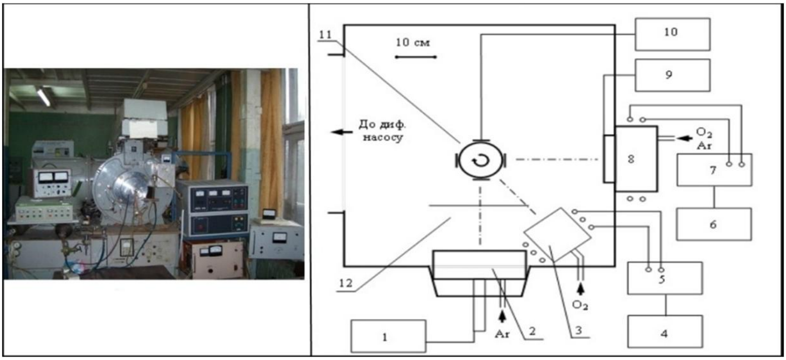
One of the most productive methods of obtaining oxide coatings are the methods of plasma-detonation and detonation deposition, which provide sufficiently thick (300-400 μm) layers of Al_2O_3, as well as with a low concentration (density) then, from 0.5 to 2.5%, and high enough adhesion of the coating to a substrate of steel.

The method of micro-arc oxidation allows obtaining of aluminum oxides on the Al samples or alloys of aluminum. This method is high-efficient and economical, but in the coatings obtained by this method, there are pores and very difficult to get coating of Al_2O_3 without impurities [3].

Therefore, there is a problem to get high-quality coatings of Al_2O_3 (without additives) with high heat-shielding properties, high hardness and good adhesion to the substrate steel. This problem is being solved in this work. But in order to evaluate the influence of substrate on the mechanical properties of Al_2O_3 coatings, they were deposited on nanostructured thin layer of TiN.

EXPERIMENTAL STUDIES

Aluminum oxide coatings were prepared on installation URM-3 by magnetron sputtering, which allows good control over strength, elastic modulus, adhesion and physical properties of the coating [4]. The photo and scheme of URM-3 is shown in *Fig. 1* [5]. To obtain coating the magnetron (2) was used, which is fed from a source (1). Power supply for the magnetron produces the voltage to 1 kV and discharge current to 20 A, the maximum power of the power supply – 6 kW.



a) b)

Fig. 1 a) General view of the reactive synthesis of coating unit on the basis of a magnetron plasma sources and ion HF; b) The scheme of the reactive coating synthesis unit

Target magnetron with the diameter of 190 mm made of aluminum. Distance from the target to the samples can be changed within 100-700 mm in the case of magnetron sputtering only, and is fixed at about 300 mm, in the case of both the magnetron and ion source.

The unit is schematically shown in Figure 1 (b). It consists of the low-pressure magnetron (2), located on the opposite end of the chamber lid, the RF plasma source and the active particles jet of gas (3) is located inside the chamber, (5) - (7) - a matching device; ion source (8) is located on the side flange of the chamber. The relative position of these elements is chosen in order to let the treated surface simultaneously feed stream of metal particles of activated reactive gas and ions of inert or reactive gases.

The coatings deposited on steel specimens (12X18H10T, Ø 20 mm, δ = 4 mm), as well as witnesses samples (glass substrate). The evaporated material was aluminum 999. Before coating, the metal specimens were grounded, polished, and then together with the samples, witnesses were treated in the ultrasonic bath for 100 seconds with output power 50 W. Technological parameters of deposition are shown in *Table 1*. The thickness of coatings Al_2O_3 is 1.25 - 1.5 μm.

Table 1 – Physical-technological parameters of coating deposition Al_2O_3

Coatings	Cleaning (inductive discharge)					Deposition				
	P, Pa	P_{magn}, W	U, V	I_{shift}, mA	τ, min	P_{Ar}, Pa	Q (acid), cm^3/ min	P_{gen}, Pa	U, V	I, A
Al_2O_3	0,07	500	300	2,5	20	0,078	24	0,083	650	7,7

RESULTS AND DISCUSSION

A good coating should have an effective resistance to abrasion, adhesion, corrosion-oxidative and other types of wear, both at room and elevated temperatures. To determine these properties it is necessary to take into account a lot of data. Among them: the elemental composition of the coating, its hardness, topography, roughness, adhesion, deformation, etc. [6], [7].

Surface topography of coatings was studied on witnesses samples (glass substrate) using the atomic force microscope (AFM). AFM is designed for study and research of the surface topography to obtain 3D image of the surface with a resolution of 0.01 nm.

To determine the initial surface roughness of the samples, the automated high-precision contact profilometer SURTRONIC 25 was used. It allows quick and accurate determination of the surface roughness.

X-ray diffraction studies were carried out on DRON-3 diffractometer in filtered Cu-Ka radiation. X-ray diffractometer gets the phase analysis of polycrystalline objects and study of textures, the orientation of the single-crystal blocks, gets the full set of intensities of reflections from single crystal to investigate the structure of many substances in various environmental conditions, etc.

Investigation of the hardness of the samples coated with Al_2O_3 was conducted by the triangular Berkowitz indenter on the nanotverdometer Nano Indenter G200. The accuracy of the depth measuring of indentation ± 0,04 nm. Measurements of the samples were carried to the depth of 100 nm to avoid contributions to the measured hardness of the substrate composition of the film-substrate, which does not exceed 1/10 of the film thickness. Tests were conducted using the console CSM (continuous stiffness measurement), which allows continuous monitoring of the stiffness of the contact in the implementation of the indenter.

The tests were performed at a constant rate of deformation in the contact, and it is equal to 0.05 s^{-1}. At least 6 prints at distance 15 μm from each other were applied to each sample. The technique by Oliver and Farr was applied to find the hardness and elastic modulus. Before testing the sample, the fused silica was tested, which is the standard of hardness in nanoindentation. The resulting value for fused silica hardness allows judging the reliability of the calibration of nanotverdometer.

To determine the adhesive/cohesive strength of coatings and to determine the mechanism of destruction the scratch-tester REVETEST (CSM Instruments) was applied. To determine the adhesive strength of coating the diamond spherical indenter of the "Rockwell C» with radius of curvature 200 mm continuously scratched the surface at an increasing load, and registered the physical parameters: acoustic emission, friction coefficient and the penetration depth of the indenter. At a certain critical load coating starts to break down. Critical loads are accurately recorded by the acoustic sensor, attached to the shoulder of loading, but also can be detected via built-in optical microscope.

The critical load is used as a quantitative assessment of adhesion of micro- and nanofilms, coatings, and combinations of layers.

Tests were carried out under the following conditions: the load on the indenter increased from 0.9 to 70 N, the speed was 1 mm/min, the length of scratches was 10 mm, loading rate - 6.91 N/min, the frequency of the signal discretization - 60, acoustic emission - 9.To obtain reliable results, we applied two scratches on each sample.

The surface morphology of Al_2O_3coatings

The quality of preparation of the coating surface was investigated by using profilometer. *Figure 2* shows the original surface profilograms samples.

The results of profilogram processing show that the average surface roughness R_a is 0.088 μm. The surface roughness of Al_2O_3 changed after the coating process.

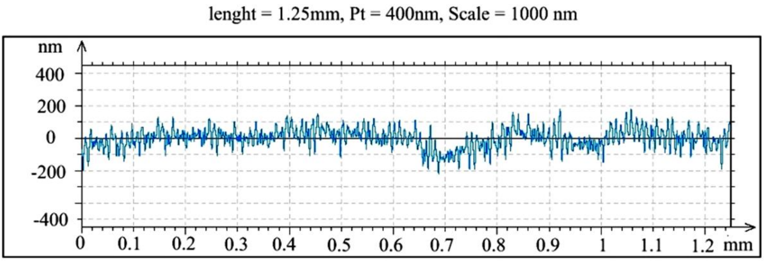


Fig. 2 – Profilogram of initial surface samples 12X18H10T.

Comparison of the results of Al_2O_3 surface topography and surface morphology of coatings on titanium nitride base research shows that the roughness of coatings TiN (R_a = 2.6989 nm) obtained under the same physical and technological parameters of deposition, as in the magnetron sputtering (R_a = 0.9867 nm) is much higher.

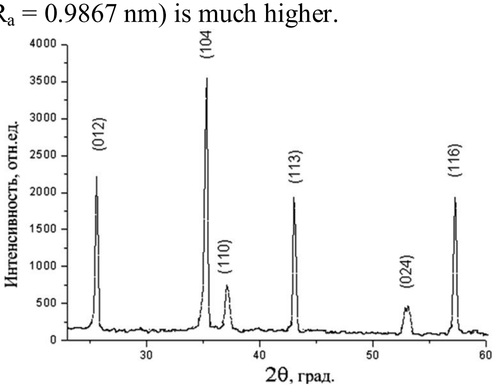


Fig. 3 – Fragments of the Al_2O_3 film diffractogram

This is due to the fact that in vacuum-arc deposition method the deposited surfaces contain a large number of droplets of evaporated material (the cathode).

The results of the phase composition research of Al_2O_3coatings are shown in *Fig. 3*. These results of X-ray analysis show that the only phase which is formed is the Al_2O_3 phase.

The mechanical characteristics of Al_2O_3coatings

The hardness of coatings deposited on steel substrate was H = 11.05 GPa, and Young's modulus E = 193 GPa.

According to [8] the mechanical characteristics (hardness) of the substrate influence on the hardness of coatings. To get the information on the effect of substrate on the hardness of coatings we conducted the following studies. Al_2O_3 coating was deposited directly on the steel substrate and the substrate, which was previously coated by hard coating based on titanium nitride by vacuum-arc method.

The results of hardness measurements of Al_2O_3 coatings, deposited on a steel substrate, with the solid titanium nitride (TiN) surface, demonstrated the increase of the hardness and Young's modulus: H = 26.07 GPa, E = 294.4 GPa.

The mechanical properties of the coatings strongly depend on the ratio of hardness (H) to the reduced Young's modulus (E*) H/E* [9]. To increase the resistance to elastic deformation of the destruction and to reduce plastic deformation of the material, it should have high strength with low elastic modulus. Analysis of these values for some materials shows that this ratio can reach 0.14. One of the parameters characterizing the structural state of the material is viscoplastic criterion. The viscoplasticity for all types of the materials, studied in the massive state does not exceed the value of 0.04.

With size of nanocrystallites decreasing below a certain critical value, the hardness and resistance to elastic deformation of the material increases. In this case, the limiting mechanism of nanostructured films deformation becomes the diffusion mass transfer, whereas the movement of dislocations is hindered by the small crystallite size and by the presence of intergranular amorphous layers. The N/E* value of our Al_2O_3 coating was 0.057, which characterizes the state of the material as fine grained. And the N/E* of Al_2O_3 coating, deposited on a substrate with the intermediate layer of titanium nitride, was 0.08, which characterizes the state of the material as nanocrystalline. Thus, it can be concluded that depositing Al_2O_3 on the surface of the substrate with a hard surface, enhances the hardness of the material.

Bond strength of ion-plasma coatings Al_2O_3

The process of destruction and the strength of adhesion of coatings formed in the substrate were analyzed by the Scratch-test method. When scratching the material with a low H/E it is naturally to expect establishing of contact in a pair of elastic friction, while the flow of plastic deformation is less likely. *Figure 4* shows photographs of the scratches of Al_2O_3 coating and results of tests for adhesive strength.

Comparative analysis of the coatings indicates that coating wears out during the scratching, but do not peel, which means that it is not destroyed by the cohesive mechanism associated with plastic deformation and the formation of fatigue cracks in the coating [15,16].

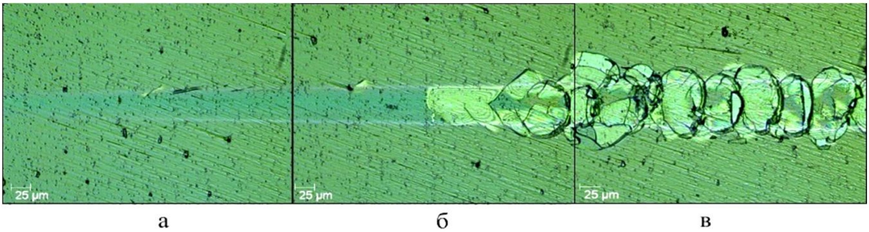


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Fig. 4 – Photos of Al_2O_3 coatings scratches at different loads on the indenter: a - 6.19 N load, b - load 10.83 N; c- load 16.65 N

The analysis of Al_2O_3 coating scratches indicates that under the load P = 6.19 N there are no cracks appearing on the coatings surface (Fig. 4a). With further increase in load at P = 10.83 N the coating is becoming chipped (Fig. 4b). Then, when the load P = 16,65 H (Fig. 4c) the coating starts to destruct.

The process of destruction of Al_2O_3 coatings by scratching with a diamond indenter with the account of changes in acoustic emission, friction coefficient, penetration depth can be divided into three stages, see Figure 5.

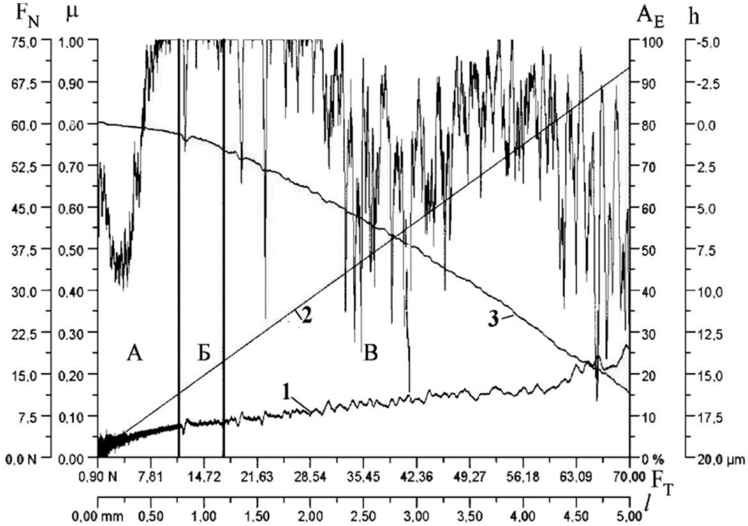

Fig. 5 – Results of adhesion tests of Al_2O_3 coating: 1 - coefficient of friction, and 2 - the value of the normal load, 3 - depth of penetration of the indenter, 4 - the value of acoustic emission

At the beginning of the process (A) the indenter is monotonously penetrate into the coating, and the coating has a substantial resistance to penetration of the indenter, the coefficient of friction (μ) monotonically increases, the signal of acoustic emission (A_e) remains practically unchanged. Then, with increasing load (B) the level of amplitude A_e begins to change, but also slightly changes the value of the friction coefficient, while the penetration depth remains practically unchanged. With further increase in load (B) is a slight increase in friction coefficient, penetration depth increases and there is a destruction of coatings.

CONCLUSIONS

The detailed analysis of Al_2O_3 coatings shows that by manipulating of different regimes and parameters of deposition there can be obtained films with excellent physical and mechanical properties. The obtained coatings demonstrated enhanced hardness and wear resistance, and also good adhesion to substrate. It is also important to note, that the material of substrate effects on hardness of coating, which is demonstrated in this work.

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