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INVESTIGATION OF THE ADHESION STRENGTH AND CORROSION RESISTANCE OF THE COATING BASED ON ALUMINUM OXIDE AND ZIRCONIUM OBTAINED BY THE DETONATION METHOD

ДЕТОНАЦИЯЛЫҚ ӘДІСПЕН АЛЫНҒАН АЛЮМИНИЙ МЕН ЦИРКОНИЙ ОКСИДІ НЕГІЗІНДЕГІ ЖАБЫННЫҢ АДГЕЗИЯЛЫҚ БЕРІКТІГІН ЖӘНЕ КОРРОЗИЯҒА ТӨЗІМДІЛІГІН ЗЕРТТЕУ

ИССЛЕДОВАНИЕ АДГЕЗИОННОЙ ПРОЧНОСТИ И КОРРОЗИОННОЙ СТОЙКОСТИ ПОКРЫТИЯ НА ОСНОВЕ ОКСИДА АЛЮМИНИЯ И ЦИРКОНИЯ ПОЛУЧЕННОГО ДЕТОНАЦИОННЫМ МЕТОДОМ

Abstract. *In this work,* Al_2O_3 *and* ZrO_2 *powders were applied to the substrate surface by the detonation method, a structural analysis of the cross section of the obtained coatings and an EDC analysis were carried out. The effect of temperature on the structural-phase exchange is considered, the adhesion and tribomechanical strength of* Al_2O_3 *and* ZrO_2 *coatings is checked, their resistance to corrosion in NaCl and 0.5 molar acid* H_2SO_4 *is determined. It was found that the value of the abrasive wear coefficient K in the* Al_2O_3 *coating is more than 2 times, the value of the* ZrO_2 *coating is more than 1.5 times, that is, the abrasive wear resistance of* Al_2O_3 *and* ZrO_2 *coatings obtained by detonation method. It was found that the* Al_2O_3 *coating is 1.5 times more resistant to corrosion than the substrate, and the* ZrO_2 *coating is about 10 times more resistant to corrosion.*

Keywords: *detonation method, coating, corrosion, structure, coefficient of friction, tribology, adhesion, microhardness.*

Аңдатпа. *Жұмыста* Al_2O_3 *және* ZrO_2 *ұнтақтары детонациялық әдіспен төсеніштің (подложка) бетіне жағылды, Алынған жабындардың көлденең қимасынан құрылымдық талдау жасалып, ЭДС талдау жасалды. Температураның құрылым-фазалық алмасуға әсері қарастрылды,* Al_2O_3 *және* ZrO_2 *жабындардың адгезиялық және трибомеханикалық беріктігі тексеріліп, NaCl және 0.5 молиярлы* H_2SO_4 *қышқылында коррозияға тұрақтылығы анықталды.* Al_2O_3 *жабынындағы абразивті тозу коэффициентінің мәні 2 еседен астам,* ZrO_2 *жабынының мәні 1,5 еседен артық екендігі, яғни детонация әдісімен алынған* Al_2O_3 *және* ZrO_2 *жабындарының абразивті тозуына төзімділігі анықталды. Төсеніш материалмен салыстырғанда* Al_2O_3 *жабыны 1.5 есе,* ZrO_2 *жабыны 10 есеге жуық коррозияға тұрақты екені анықталды.*

Кілттік сөздер: *детонация әдісі, жабын, коррозия, құрылым, үйкеліс коэффициенті, трибология, адгезия, микроқаттылық.*

Аннотация. *В данной работе порошки Al_2O_3 и ZrO_2 наносились на поверхность подложки детонационным методом, проводился структурный анализ поперечного сечения полученных покрытий и ЭДС-анализ. Рассмотрено влияние температуры на структурно-фазовый обмен, проверена адгезия и трибомеханическая прочность покрытий из Al_2O_3 и ZrO_2, определена их коррозионная стойкость в NaCl и 0,5 молярной кислоте H_2SO_4. Установлено, что значение коэффициента абразивного износа K в покрытии Al_2O_3 более чем в 2 раза, значение покрытия ZrO_2 более чем в 1,5 раза, то есть сопротивление абразивному износу покрытий Al_2O_3 и ZrO_2, полученных детонационным методом. Было обнаружено, что покрытие из Al_2O_3 в 1,5 раза более устойчиво к коррозии, чем подложка, а покрытие из ZrO_2 примерно в 10 раз устойчивее к коррозии.*

Ключевые слова: *детонационный метод, покрытие, коррозия, структура, коэффициент трения, трибология, адгезия, микротвердость.*

Introduction. Currently the surface of the piping elements of the boilers of thermal power plants or the blades of the steam turbines are often damaged by high temperatures and steam pressure. The damage caused by accidents results in the enormous damage to boiler parts. This has a direct impact on all other fields of society and creates a major economic crisis. Any (special) super alloys applied to the parts of the boiler corrode over time under the influence of high temperatures and pressures and lose their physical, mechanical and tribological properties. In order to prevent these shortcomings, in recent years, instead of inventing new materials, scientists have focused on the development of new coating technologies that improve the surface properties of metals and alloys and study the properties of the obtained coatings [1-4]. Coatings are widely used in automotive parts, boiler components, chemical process and medical equipment, aircraft engine elements, surface and offshore turbines, in the shipbuilding industry, etc. [5-7]. Thermal spraying, which is one of the technologies of surface treatment, is a cheap way to improve the surface properties of metal particles, to obtain a thick and high-quality coating. Among the thermal spraying methods are detonation spraying (DS) and high-velocity oxide spraying (HVOS), which allows to obtain a hard, dense and wear-resistant coating with excellent adhesive strength, low porosity and compressive residual stresses [8-12]. At the same time, the initial powder causes minimal oxidation of the material and provides high speed and relatively low temperature [13-15]. The sprayed powder particles adhere to the substrate at a speed of 800-1200 m/s under the influence of detonation waves [16]. The quality of detonation coatings is directly related to the surface roughness of the pavement material (degree of processing), the chemical composition of the pavement material, the size of the granules, the ratio of gases that cause detonation explosions, impurities. In The problems require further study, as the physical-mechanical, tribological properties and formation of the phase structure of various coatings obtained by detonation and other spraying methods have not yet been fully studied. Therefore, The aim of this work is to study the effect of temperature on the structural, phase and mechanical properties of coatings based on aluminum and zirconium oxides.

Materials and methods. Detonation spraying was employed as the method of producing Al_2O_3 and ZrO_2 coatings. Alumina powder (20-60 μm) and zirconium powder (20-80 μm) were used. Spraying was carried out using a CCDS2000 detonation gun with an 800 mm long 20 mm diameter barrel (fig. 1), installed in the Research Centre for Surface Engineering and Tribology, Kazakhstan. The distance between the barrel and the sample was 250 mm. Samples made of titanium-alloyed austenitic stainless steel 12Ch18N10T, corresponding to steel AISI 321, were used as the substrate for coating deposition.

Figure 1. Diagram of the detonation spraying unit "CCDS-2000"

The chemical composition of the tested steel is specified in standard GOST 4986-79 **[**17]. The steel samples’ dimensions were 75x50x5 mm and their roughness was *Ra* = 0.088 µm. First the substrates were chemically cleaned for 7-10 minutes. Then the dried substrates were sandblasted (using Contracor Eco140S, Germany) with electrocorundum with a grain size of about 300 µm to achieve an average roughness of 4.5 µm. When obtaining the aluminum oxide coating, the filling of the shaft with gases (C_2H_2/O_2) was 71%, the filling of the dispenser with powder was 66%, the surface roughness of the obtained coating was 5.10 µm.

Surface morphology, refractive index, and friction pathways were studied using Phenom ProX raster electron microscope (Phenom-World BV, Netherlands). The elemental composition of the coatings was analyzed by characteristic X-ray spectra using an X-ray energy dispersion spectrometer (EDS) located inside a microscope. X-ray diffraction study of coated samples was performed on Xpert PRO diffractometer (U = 40kv, I = 30mA CuKα) in point scanning mode with a step of 2θ = 0.02 degrees (PANalytical, Netherlands). The hardness of the coatings was measured using a Vickers instrument for measuring microhardness DuraScan-20. The innovative load range from 10 gf to 62 kgf greatly expands the field of use. for each position an average value was obtained, measured 3 times from the coating surface to ensure the accuracy of the experimental data. Anton Paar scratch testers were used to determine the adhesion of the coating, resistance to scratches and damage. The experimental process as follows: the initial load of the indenter is 0.01 N, and it is loaded from 0.01 N to 30 N at the loading rate of 29.99 N/min. The slip speed is 6.79 mm/min and the scratch length is 7 mm. The critical load (Lc) was estimated by the acoustic signal. And the critical load referred as the load that the interface between coating and substrate begins to separate. Therefore, for showing the adhesive properties of the coating more intuitively, the testing instrument of SEM and was used. Tribological tests were performed in the air on a friction machine "Tribometer TRB^3" (CSM Instruments, Switzerland) by the "ball-disk" scheme. A ball made of 100Cr6 certified material with a diameter of 6.0 mm was used as counterbody. The load was 10 N and the rotational speed is 10 cm/s. Test conditions comply with international ASTM G99-959 and DIN50324 standards. Cross-section roughness of the sample was determined using Profilometer 130. The structure of the trace of the ball on the surface of the coating was studied using Neophot-21 optical microscope.

Results and discussion. The surface structure of the cross section of the coating is shown in Figure 2. The study of surface morphology reveals an increase in the thickness of the layer, a decrease in surface roughness, which is characteristic of the detonation method. Point elemental analysis of the cross section of the coatings was performed (Figure 3).

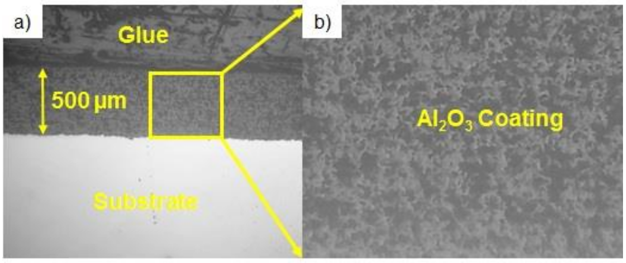

Figure 2. Surface structure of Al_2O_3 coatings obtained by detonation:
a) Cross-sectional structure b) surface structure obtained from the coating

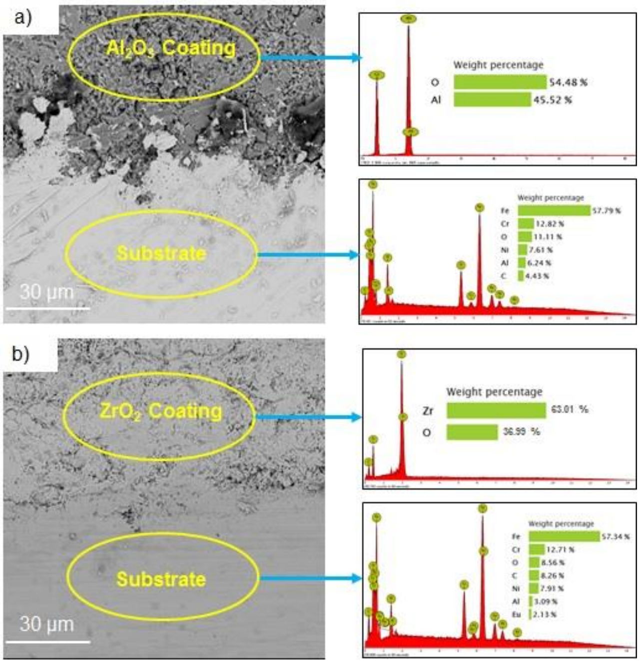

Figure 3. SEM image and EDS analysis of Al_2O_3 and ZrO_2 coating:
a) Cross-sectional structure (Al_2O_3); b) surface structure obtained from the coating (ZrO_2)

During detonation, the elements of the gas mixture are not on the surface of the coating. It was shown that the elemental composition of the main coating surface is Al_2O_3, and the light strip on the surface contains Fe, Cr, Ni, Al, C, O, according to the results of elemental analysis. The presence of Fe, Cr, Ni comes from the substrate, i.e. the impurities accumulated in the hollows on the surface during polishing of the sample.

[18-21] stated that the powder based on Al_2O_3 has the ability to undergo several modifications under the influence of high temperatures. Also, the composition of the Al_2O_3 coating during thermal spraying is α, γ, δ, θ, and different phases, of which the formation of α and γ phases is predominant.

Table 1. The result of the adhesive test of Al_2O_3 and ZrO_2 coatings

Critical load	Coating

	Al_2O_3	ZrO_2
L_{C1}	4.57	11.06
L_{C2}	8.98	16.32
L_{C3}	25.24	26.28
L_{C4}	28.61	29.65

Table 1 shows the results of testing the Al_2O_3 and ZrO_2 coating for adhesion strength. Adhesion strength refers to the critical load value L_C, which has a more informative characteristic during abrasion of the sample during testing (Figure 4). Comparison of surface profiles with polished steel discs (substrate) and Al_2O_3 coating deposition, detonation explosion temperature (volume of shaft gas filling), spraying speed, size of alumina powder, distance between the shaft and lining material, etc. leads to an increase in the surface roughness.

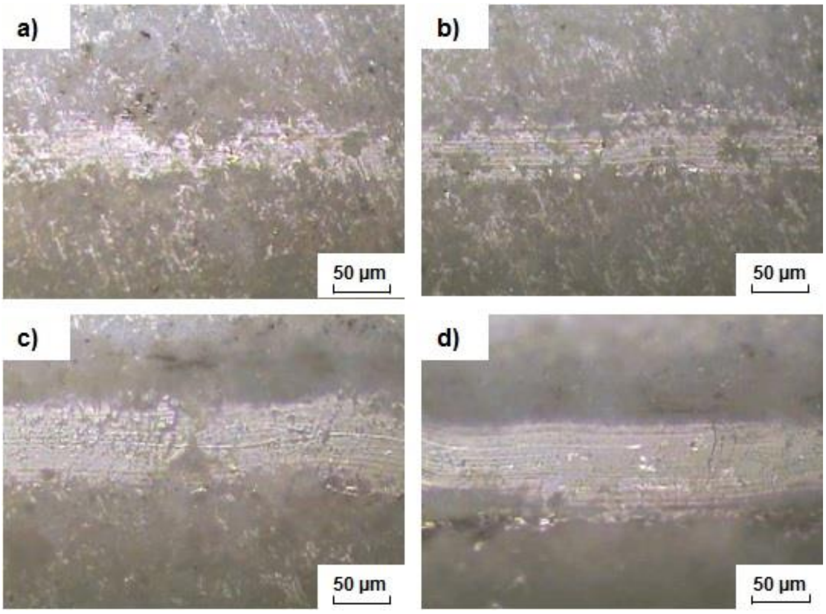

Figure 4. Microphotograph of the area in contact with the diamond indenter during scratch testing of Al_2O_3 coating (Fig. 6): a – region 1; b – region 2; c – region 3, d – region 4

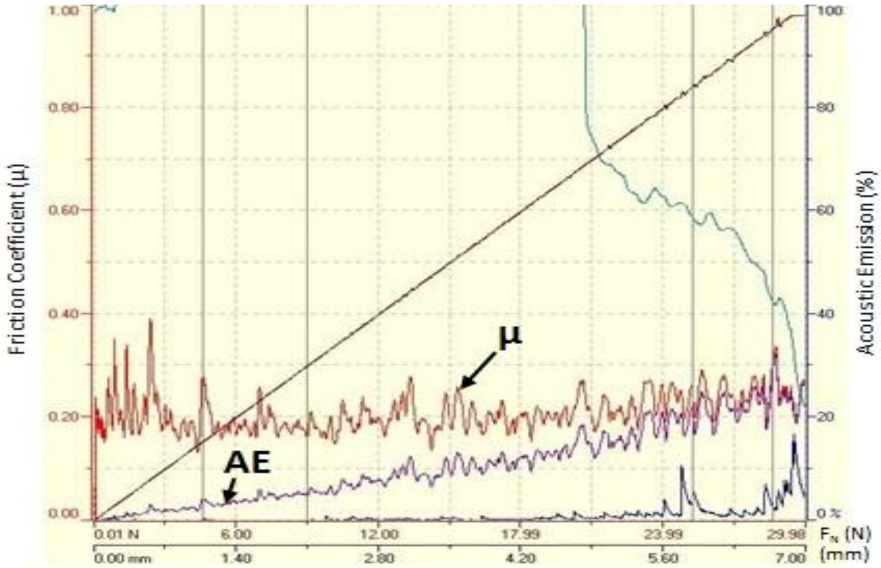

Figure 5. Correlation between the coefficient of friction under load and acoustic emission signal used in scratch testing of Al_2O_3 coating

The results of the study of adhesive-cohesive strength and scratch resistance are shown in Figures 5 and 6. Characteristic values of the critical load were determined by the change in the values of the coefficient of friction and acoustic emission signal with increasing scraping load (Fig. 4) L_C: L_{C1} - the appearance of the first chevron crack at the bottom; L_{C2} - the appearance of numerous chevron cracks at the bottom of the cracks and the local peeling of the coating, the appearance of chevron cracks at the bottom of the cracks; L_{C3} - cohesion-adhesion damage of the coating; L_{C4} - plastic abrasion coating. For the criterion of adhesive strength, the value of L_{C4} of the critical load at which the coating is rubbed was adopted.

According to these criteria, the process of destruction of the coating when drawn with an indenter can be divided into four stages. Monotonic penetration of the indenter into the coating in the load range from F = 0.70 N to 4.57 N, with a slight increase in the coefficient of friction, and the acoustic emission signal remains unchanged. At the load of F = 8.98 N, the indenter is completely immersed in the coating, and the diamond indenter with a coefficient of friction of 0.35 slides over the coating. As the load increases (F = 25.2-28.6 N), the compression of the material in front of the indenter in the form of a bump and the depth of penetration of the indenter increases.

The substrate and the surface of the Al_2O_3 coating after tribological examination were photographed using Neophot-21 optical microscope, the surface of the substrate and the Al_2O_3 coating with a 6 mm diameter 100Cr6 ball at a speed of 2 cm/s and a vertical force of 10 N. A trace of 4000 revolutions was made on the surface of the sample, and the depth of friction of the trace was determined using "Profilometer 130". The average value of the coefficient of friction of the tribological test on the floor was $\mu \approx 0.669$, the depth of the groove was h = 8.82 μm. The average value of the coefficient of friction of the coating coated with alumina powder was $\mu \approx 0.603$, the depth of the groove was h = 0.44 μm. In comparison, there is not much difference in the coefficient of friction of the substrate and the coating, but in the depth of the groove the coating is 20 times less abrasive, i.e. the detonation of the coating leads to abrasion (wear).

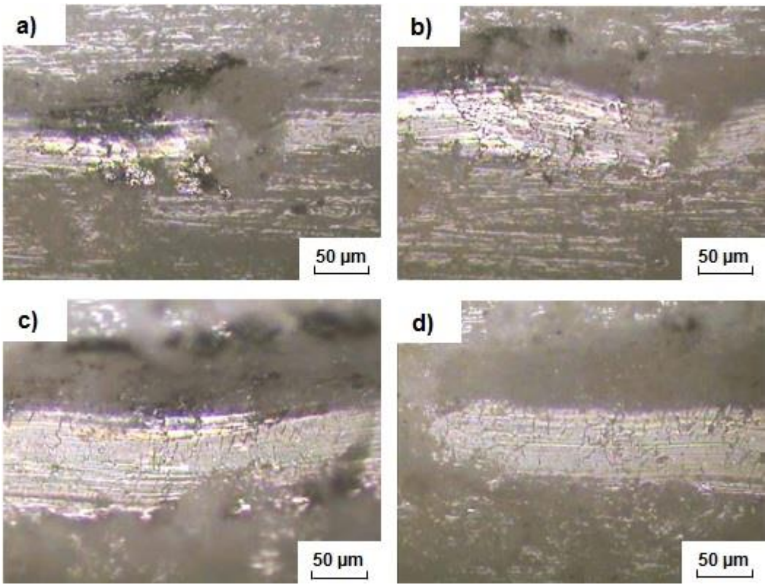

Figure 6. Microphotograph of the area in contact with the diamond indenter during scratch testing of ZrO_2 coating: a - region 1; b - region 2; c - region 3, d - region 4

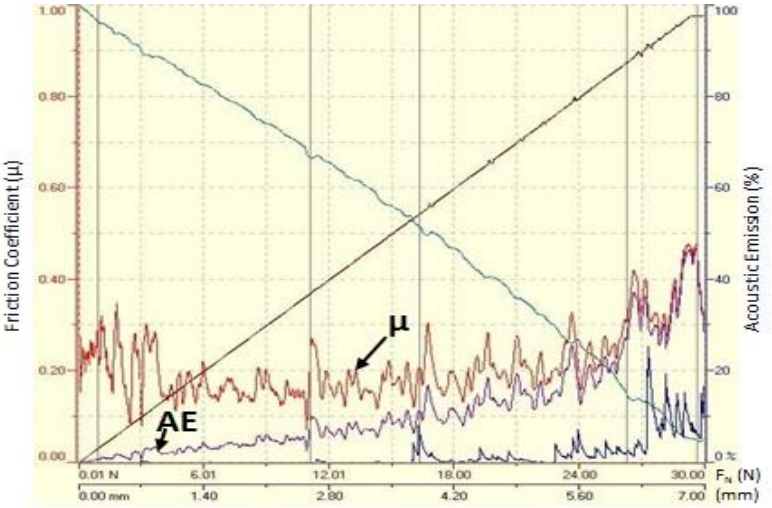

Figure 7. Correlation between the coefficient of friction under load and acoustic emission signal used in scratch testing of ZrO_2 coating

Table 2. The result of the abrasion and corrosion resistance of the coatings

Sample	Steel 40X	Substrate	Al_2O_3 Coating	ZrO_2 Coating
$\Delta W_{[c]}$	0.0308	0.0314	0.0275	0.0266
K	1	0.968	2.189	1.59
R_{corr} (cm/ Year)	-	0.928	0.737	0.586
NaCl acid				

H_2SO_4 acid	-	1.540	0.928	0.147

According to these criteria, the process of destruction of the coating when drawn with an indenter can be divided into four stages **(**Fig. 6). Monotonic penetration of the indenter into the coating in the load range from F = 0.60 N to 11.06 N, with a slight increase in the coefficient of friction, and the acoustic emission signal remains unchanged. At the load of F = 16.32 N, the indenter is completely immersed in the coating, and the diamond indenter with a coefficient of friction of 0.26 slides over the coating. As the load increases (F = 26.2-29.6 N), the compression of the material in front of the indenter in the form of a bump and the depth of penetration of the indenter increases **(**Fig. 7).

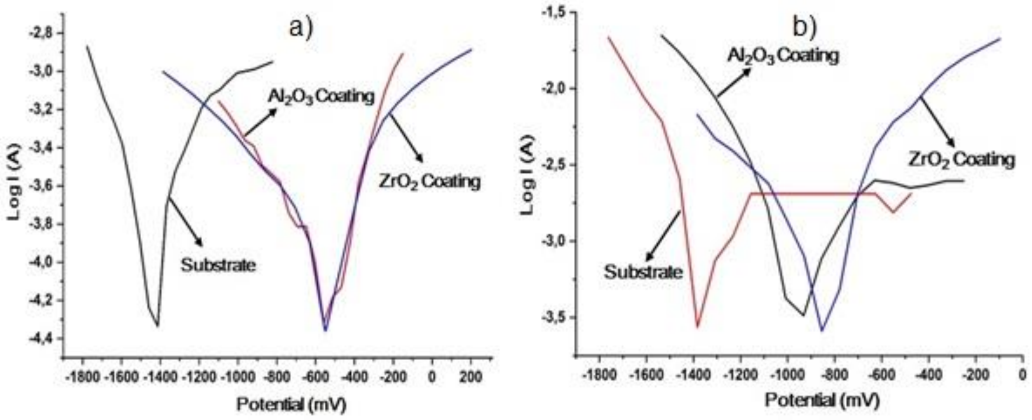

Figure 8. Relative graph of the corrosion resistance of the substrate material, Al_2O_3 and ZrO_2 coatings versus potential (E) and current (Log I): *a) NaCl acid b) H_2SO_4 acid*

Figure 8 shows the results of the study of the substrate Al_2O_3 and ZrO_2 coatings in NaCl acid and 0.5 molar H_2SO_4 acid (Fig. 8, b) in the relative form of the substrate (Fig. 8, a) (Table 2). It was found that the value of the abrasive wear coefficient K in the Al_2O_3 coating is more than 2 times higher than in the coating material, and the value of the ZrO_2 coating is more than 1.5 times, ie Al_2O_3 and ZrO_2 coatings obtained by the detonation method are resistant to abrasive wear. With the help of potentistat we see that the annual corrosion rate in NaCl acid decreased from 0.928 in the substrate Rcorr (cm/year) to 0.737 in the Al_2O_3 coating and 0.586 in the ZrO_2 coating. ZrO_2 in the coating decreased by 0.147, the results of the corrosion study showed that the coatings are quite resistant to acid. It was found that the Al_2O_3 coating is 1.5 times more resistant to corrosion than the substrate, and the ZrO_2 coating is about 10 times more resistant to corrosion.

Conclusions. Thus, the obtained theoretical and experimental results of the study are a new step in solving the problem of creating protective coatings based on Al_2O_3 and ZrO_2, structural and phase characteristics of which allow to increase the durability of various critical parts operating at high temperatures, loads, pressures and aggressive environments.

1. The mechanical and tribological properties of Al_2O_3 powder were significantly increased by spraying Al_2O_3 powder on the substrate using CCDS-2000. X-ray phase analysis of Al_2O_3 powder consisted of R-3c hexagonal α-lattice, and semi-γ-phase lattices were formed after detonation spraying.
2. The result of scratch testing of the coating was determined by the relationship between the coefficient of friction and the acoustic emission signal, and for the criterion of adhesion

strength was determined L_{C4} value of the critical load at which the coating is rubbed.

3. It was found that the value of the abrasive wear coefficient K in the Al_2O_3 coating is more than 2 times, the value of the ZrO_2 coating is more than 1.5 times, that is, the abrasive wear resistance of Al_2O_3 and ZrO_2 coatings obtained by detonation method.

4. The annual corrosion rate in NaCl acid decreased from 0.928 in the AlcO3 coating to 0.737 in the Al_2O_3 coating and from 0.586 in the ZrO_2 coating in the Rcorr (cm/year) substrate, the annual corrosion rate in the H_2SO_4 acid from Rcorr in the substrate from 1.540 to 0.9 It was found that the Al_2O_3 coating is 1.5 times more resistant to corrosion than the substrate, and the ZrO_2 coating is about 10 times more resistant to corrosion.

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