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Experience in Detonation Nano-Structures Coating Application Technologies using Condensed Explosives and Gas Mixtures

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Abstract

Objectives: The article gives an insight to reviews and research in detonation nano-structured coating, using condensed explosives and gas mixtures applied at the SamSTU and other facilities in the Samara region. **Methods:** The detonation method allows obtaining nanostructured composite materials and coatings that are unique in their physical and mechanical properties. Detonation sputtering is a coating technology that relies on gas explosion energy for heating and accelerating a powdered material. **Findings:** The experience of industrial use of wear-resistant detonation coatings and possible applications has been demonstrated. According to our research, it is possible to raise surface hardness of specimens by more than 3 times and 2 to 10 times with wear resistance. It is shown that the suggested technology ensures higher stability of mechanical properties of coatings. Thus, original hardness of steel specimens was in the range of 400 to 600 kgf/mm^2. Hardness values of detonation-sputtered hard-alloy coatings were ca. 1,200 to 1,400 kgf/mm^2 and activation energy was up to 350 kJ/mole, which is typical of hard-alloy materials. Scratch-hardness tests showed rather high coating and base material adhesion values. According to the preliminary data, shear strengths over 150 MPa may be achieved. Thus, aluminum-substrate Al_2O_3 strength was 163 MPa and aluminum-substrate and Ti-subcoat Al_2O_3 strength was 152 MPa. **Novelty/improvements:** The suggested novel method enables to increase projection velocity of powdered materials and creates an extra heat effect giving plastic properties to the injected materials.

Keywords: Adhesion, Cohesion, Detonating Gas Mixture, Detonation Sputtering, Explosives, Hardness

1. Introduction

Improving robustness of modern technical devices, reducing maintenance costs, ensuring competitive performance, extending service life and restoring function of worn units up to new devices is the most desirable machine development trend. The use of protective coating application technologies is the primary way to solve this problem. Actual strength of metal materials can be increased significantly by converting such materials into a sub-microcrystalline or nano-crystalline state. There are different techniques available to achieve a high-strength nano-crystalline state in metals and alloys. However, difficulties in developing the even nano-structure for high volumes of construction materials and preserving such structure in joints of elements make development of the technologies and broad commercial exploitation of nano-structuring of surface layers and coatings of modern construction and tooling materials relevant.

Now, production of powders of grain size less than 100 nm that may be used for creating reinforcing nano-structured coatings has been mastered at domestic and foreign organizations.

It is well known that a reduction in the grain size of applied coatings leads to a significant increase in piece performance[1]. For example, a decrease in the WC grain size even in the micrometric range comes with a noticeable increase in wear resistance, hardness and

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growth in compression and flexing strength. A shift to a nano or sub-microcrystalline WC state is followed by an even higher increase in such properties (2 to 3 times).

Detonation is one of the most popular and effective techniques of protective coating; this method relies on high-velocity projection of pulverized powdered material with pin-point gas mixture explosives. At the same time, according to laboratory and full-scale testing of pieces with detonation coatings that are applied using the existing technologies, insufficient stability of mechanical properties and, in some cases, adhesion of the coating is achieved, which prevents these surface reinforcing techniques from broad implementation.

Detonation sputtering is a coating technology that relies on gas explosion energy for heating and accelerating a powdered material. The coating is applied with a detonation gun, where explosion products run temperatures up to 4,000°C and are fired at velocities over 1 km/sec. This gas flow heats particles of the powder that is introduced into the barrel up to their melting point and projects them at high velocities onto a piece that is placed in front of the gun. Micro-welding happens at collision and the powder is coupled tightly with the item surface (at the molecular level). A series of shots is done to achieve the desirable surface thickness. The piece is placed with an arm in front of the barrel in order to get a greater surface worked. Advantages of this method include low coating porosity, high adhesion to the piece substrate, low heat exposure to avoid any unnecessary thermal stresses and distortion of even sophisticatedly structured thin-wall parts.

Detonation sputtering equipment has been constantly improving for the last fifty years since the first patent has been registered[2] and a variety of detonation gun modifications is used nowadays, such as, Keram 3000 (Amulet CJSC), UDN-2M (Neftestroigazizolatsia SIT PII CJSC), ADM-4D (ADM Research and Engineering Center), Korund-2, Korund-3 (NIITavtoporm JSC), Ob (Lavrentyev Institute of Hydrodynamics, Siberian Branch of the Russian Academy of Sciences), Grom (Energokhimmash CJSC) etc. They differ not only in design, but also in features. E.g. fuels limited to natural gas limit the range of sputtered materials, axial powder feed reduces significantly factor of utilization of the powder material, high-quality coating of large areas and sophisticated parts renders impossible, unless surface scanning process is clearly coordinated with pulse sputtering process.

The latest configuration of the Ob unit (1990-2000) was the first computer-aided unit[3]. In the last years, the Lavrentyev Institute of Hydrodynamics, Siberian Branch of the Russian Academy of Sciences developed Dragon computer-aided new-generation detonation complex.

This new generation is distinguished by a multi-channel gas supply system, involving six independent feed channels for two types of fuel, oxidizer and inert components and stopping flow with fast-response solenoid valves (on-off cycle in 3-4 msec). Flow characteristic is maintained stable with the help of two original inertia-free pressure equalizers. Kickback and flashback (detonation breakthrough from the barrel into supply lines) are blocked by an original double seat valve, involving damper volume blow-off at the time of inert-gas shooting. Original design of a mix and ignition chamber, including concurrent flows in circular channels at the time of project, ensures effective mixing of explosive ingredients and intensifies transition of combustion into detonation following initiation due to multiple collisions of shock waves that are generated by accelerated combustion.

Two powder dosing apparatus may be used at the same time and they perform radial feed of the exact amount of powder in the local barrel area, which ensures higher coating quality and reduces powder losses significantly, as compared to axial feeders. Powder utilization is up to 70-80 % with these dispensing apparatus. An arm-based detonation unit houses three step motor drives to scan sophisticated surfaces with a computer control system. Barrels up to 30 mm provide two-time performance improvement, as compared to 20 mm barrels. Working frequencies up to 10 Hz allow increasing productivity even more, which reaches 3 Kg/Hr when using metal powders.

2. Approach

Nano-structured coatings are applied by detonation and using condensed active additives by means of high-velocity projection in the shock wave front of a nano-structured powdered material with detonation products that are produced as a result of directed explosion of condensed explosive and gas mixture. Application of condensed active additives in the form of explosives increases projection velocity of powdered materials (up to 100%) and creates an extra heat effect giving plastic properties to the projected material. The detonation coating method has the following undeniable advantages: Application of coatings on a cold substrate made possible, as long as activation of the joint materials is ensured by the high velocity of sputtered particles; lower sensibility to original surface cleanness; mild heating of parts in coating; low coating porosity (less than 0.1%); application of a variety of materials, including metals and alloys, oxides, oxide mixtures, ceramic metal hard alloys based on tungsten, chromium and titanium carbides and carbide and metal mixtures made possible. The detonation method allows obtaining nanostructured composite materials and coatings that are unique in their physical and mechanical properties. Thus, according to the research, surface hardness of specimens can be increased by more than 3 times and wear resistance can be increased by 2 to 10 times.

Detonation coatings perform versatile functions; therefore, a great variety of methods are used to study such coatings. General requirements to detonation coatings are specified in the standard[4]. One can find description of some of common test methods in[3–7]. Coatings that are designed for aggressive environments and high thermocyclic loads are tested, using custom-designed techniques[8]. Nevertheless, researchers and engineers are mostly interested in strength (hardness, adhesion and cohesion) and friction (abrasive and erosive wear resistance, sliding friction etc.) properties of such coatings. Techniques that produce accurate data are required to determine the above properties. Hardness is usually discussed as an indirect feature of wear resistance of coatings. Coatings are usually characterized by their micro-hardness HV_{300} (measured at 300 g load) in scientific literature. Speaking of manufacturing practice, Rockwell method is applied at 150 kgf load. This method leads to unambiguity, when applied to coatings, as long as a thin coating is destroyed at high loads. With convenient dynamic hardness meters available (e.g. TEMP-4 tester), hardness of coatings can be measured now, even on large parts. For comparison, we measured hardness of coatings of self-fluxing nickel and chromium alloys and cast iron, using all the above techniques. We determined that dynamic test data within the measurement accuracy match micro-hardness measurement data (Tables 2, 3) and standard HRC hardness meter TR 5006-2 produces highly underestimated results. According to indenter footprints of hardness meter TR 5006-2 studied under a microscope, the coating is destroyed under the action of such instrument with the material pressed out sideways, which is the reason of the above mentioned distortion.

Adhesion characterizes bonding strength of the coating and substrate. We believe pin method that is described in[9] and shown in Figure 1 to be the most reliable technique for measuring the above parameter. Tensile strength of the coating material itself, i.e. cohesion, is the most adequate characteristic of wear resistance of the coating. Direct cohesion measurement method is illustrated in Figure 2 and it involves a tear test of a circular coating applied to a pair of butted cylinder elements.

Structural test data for coatings of self-fluxing alloys ПР-НХ13СР, ПР-НХ15СР2, ПР-НХ16СР3, ПР-НХ17СР4, heat-resistant alloy ПВ-Н85Ю15 and cast iron that were obtained on the Dragon detonation unit are presented in Table 1 as an example. Properties of mixed coatings of self-fluxing alloys and alloy ПВ-Н85Ю15 are also given. Due to their high density (usually, porosity is less than 1%), detonation coatings do not require any post-sputtering flowing; therefore, all the below hardness data were obtained by direct measurements on the polished coating surface.

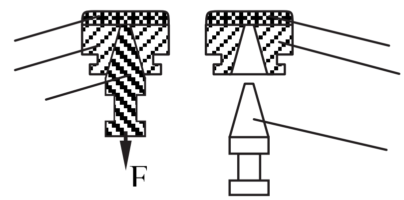

Figure 1. Measuring adhesion: 1. Taper pin, 2. Taper hole liner, 3. Coating.

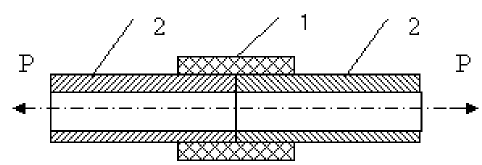

Figure 2. Measuring cohesion: 1. Coating, 2. Steel tube, P. Tensile strength.

Table 1. Structural behavior of nickel-chromium alloy and Н85Ю15 and cast iron alloy coatings

Coating	HV (dynam. method)	HRC (150 kgf)	HRC (dynam. method)	Adhesion [MPa]	Cohesion [MPa]
НХ17СР4	883	53.5	64.6	90-110	416
НХ16СР3	604	48	53.8	90-110	404
НХ15СР2	587	46.9	52.0	90-110	493
НХ13СР	451	38.6	44.3	90-110	408
Н85Ю15	560	41.6	50.5	111-120	313
80%НХ17СР4+ 20% Н85Ю15	792	52.0	61.6	100-120	458
60%НХ17СР4+ 40% Н85Ю15	746	50.5	60.0	102.4	644
40%НХ17СР4+ 60% Н85Ю15	694	47.8	58	100-120	350
Cast iron	897	52.1	64.8	93.5	331

A technique was developed to measure shear strength of coatings and it is outlined in Figure 3. Layer-by-layer measurements of shear strength of coatings and setting up of the required difference between the inner diameter of busing 1 and diameter of belt for applying tested coating 3 are the advantage of this technique. Shear tests are preferable for coatings that operate under shear loads. Moreover, the suggested technique is valuable for studying properties of gradient coatings that are now designed at the M.A. Lavrentyev Institute of Hydrodynamics of the Siberian Branch of the Russian Academy of Science. According to the preliminary data, shear strengths over 150 MPa may be achieved. Thus, aluminum-substrate Al_2O_3 strength was 163 MPa and aluminum-substrate and Ti-subcoat Al_2O_3 strength was 152 MPa.

Friction tests are done for the coatings at an abrasive and erosive bench AES that was developed at the Lavrentyev Institute of Hydrodynamics of the Siberian Branch of the Russian Academy of Science. This bench ensures abrasive test parameters as per ASTM G65, with its principles being similar to those of GOST 23.208-79. Air erosive tests are done as per ASTM G76. A flat specimen is forced in abrasive tests against a 235 mm rubber-coated disk rotating at 240 rpm with the force of 45 N.

Clamping force is 130 N for high-wearing coatings, in particular tungsten-carbide coatings. A powder-normal electrocorundum of 13A grade, grain size of 20P as per GOST 28818-90 (particle size 200-500 mkm) - is supplied onto the friction surface. Abrasive rate is 110-120 g/min. Each study is comprised of 8-10 tests, 200 disk revolutions each and the specimen if weighed on an analytical weigh following each test. Then, a wear curve is plotted and wears for 200 disk revolutions is determined. Volumetric wear is considered, which is determined by dividing the weight loss by coating material density. A wear curve for coating made of ПВ-Н85Ю15 is given as an example in Figure 4.

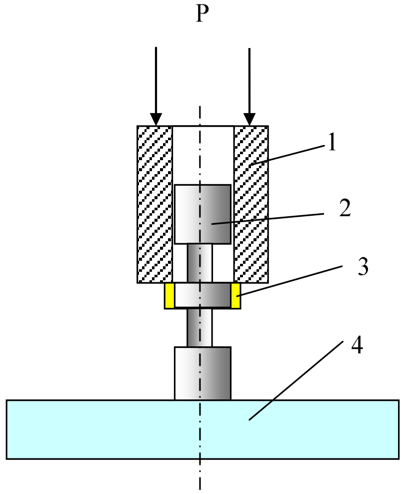

Figure 3. Coatings. Shear test configuration. 1. Liner, 2. Specimen, 3. Coating on the specimen, 4. Bench. P load on liner is shown using arrows. Inner liner diameter: 18 mm, belt diameter (under coating 3): 17.8 mm.

An air abrasive stream is fed onto the specimen from a 5 mm nozzle in erosive tests. Air pressure at nozzle input is 0.4 MPa, average velocity of abrasive parts is 65 m/sec and the distance from the nozzle to the specimen surface is 11 mm and angle between the nozzle axis and specimen surface is 60^0. Electrocorundum powder is used, which is the same as for abrasive tests. Powder rate is 1.3 g/min. Each study is comprised of 8-10 tests 5 minutes each. The specimen is weighed on an analytical weigh, following each test and weight loss is determined. Then, a wear curve is plotted (the same as for abrasive tests) and volume loss for 5 minutes is determined.

3. Results

Abrasive and erosive wear test data for coatings of the above alloys are presented in Table 2. Properties of hard-alloy WC-based coatings that were tested according to the above techniques are presented in Tables 3 and 4.

Scratch-hardness tests were done for the purpose of qualitative assessment of coating and base material adhesion. Coated specimen angle lap was scratched from the base to the coating, in which case movement of the introduced indenter simulates movement of an abrasive disc or cutter blade across the tested coated surface. And adhesion quality of the coating and base material was determined by visual examination of the coating area with the introduced indenter. No chipping or peeling of the coating off base material must be observed for adequate shear strengths of the coating.

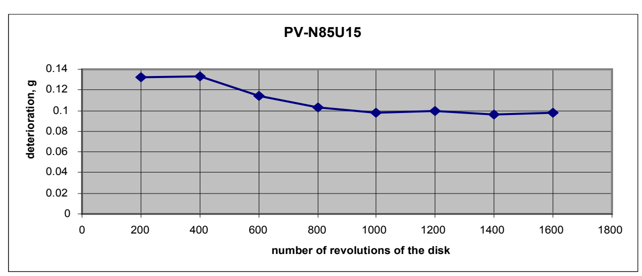

Figure 4. Abrasive wear curve for ПВ-Н85Ю15 powder coating.

Table 2. Wear and tear of nickel-chromium alloy and H85Ю15 and cast iron alloy coatings

Material	Abrasive wear [mm3/ 200 rv]	Erosive wear [mm3/ 5 min]
HX17CP4	17.1	0.79
HX16CP3	24.0	0.71
HX15CP2	24.7	0.76
HX13CP	15.3	0.62
H85Ю15	16.1	0.24
80%HX17CP4+20% H85Ю15	15.2	0.67
60%HX17CP4+40% H85Ю15	16.0	0.61
40%HX17CP4+60% H85Ю15	16.6	0.49
Cast iron	21.4	0.56

Table 4. Abrasive and erosive wear of hard-alloy coatings

Coating	Abrasive wear [mm3]	Erosive wear [mm3]
Coatings that contain 12% Co		
Diamalloy 2004	0.92	0.28
80.71.1W	0.66	0.23
Mechanomade 301	0.67	0.34
Coatings that contain 17% Co		
Diamalloy 2005 NS	1.99	0.29
Coatings that contain 25% Co		
BK-25	1.97	0.31
Coatings that contain 30% Co		
Mechanomade T308	3.35	0.45

Table 3. Adhesion, cohesion and micro-hardness of hard-alloy coatings

Coating	Adhesion [MPa]	Cohesion [MPa]	Micro-hardness [MPa]
Coatings that contain 12% Co			
Diamalloy 2004	129	199	10015
80.71.1W	149	192	10111
Mechanomade 301	150	192	10500
Coatings that contain 17% Co			
Diamalloy 2005	142	200	8860
Coatings that contain 25% Co			
BK-25	269	199	7317
Coatings that contain 30% Co			
Mechanomade T308	281	538	8723

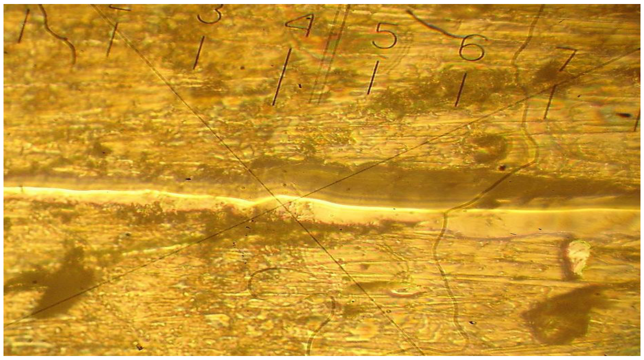

Figure 5. Footprints of diamond indenter in the transitory zone on the surface of detonation-coated specimen.

Furrows left after the transitory zone was ploughed with the diamond indenter are shown in Figure 5. Abrupt furrow narrowing in the photo indicates transition of the base material into the coating.

High performance of detonation coatings determined wide application of the detonation sputtering technology in the Samara industrial region. Detonation hard-alloy coatings have been successfully used[10,11] for reinforcing cones of three-cone (Figure 6a) and diamond (Figure 6b) drilling bits according to an agreement with the Volgaburmash JSC. A significant rise in abrasive strength of the bit, almost complete elimination of the problem of drill-through tools falling out down the hole and reduction in failures due to cones cracking is the achieved effect (for coating thickness of 200 mkm).

High strength and adhesion properties of the coatings permit the use of detonation coatings to restore dies, e.g. blanking dies for bearing cages (Figure 6c) and positive dies (Figure 6d).

Detonation coatings may come into use in automotive industry, in particular for restoring and reinforcing worn crankshaft pins (Figure 6f). High friction compatibility of hard-allow detonation coating and silver coating friction pair that was discovered in tests found use in manufacturing of balancing disks for segmental centrifugal pumps (Figure 6e). In this case, a hard-alloy coating is applied to the working surface of first disk and an anti-friction silver-diamond coating is applied to the working surface of the second disk. Detonation coatings are widely used in machine engineering for restoring worn spindles (Figure 6j). Heat-insulating aluminum oxide coatings are used for life-extending treatment of copper nozzles in welding torches (Figure 6k). Reinforcing of farming machinery, e.g. spade blades is one of the most effective applications of hard-alloy coatings (Figure 6l).

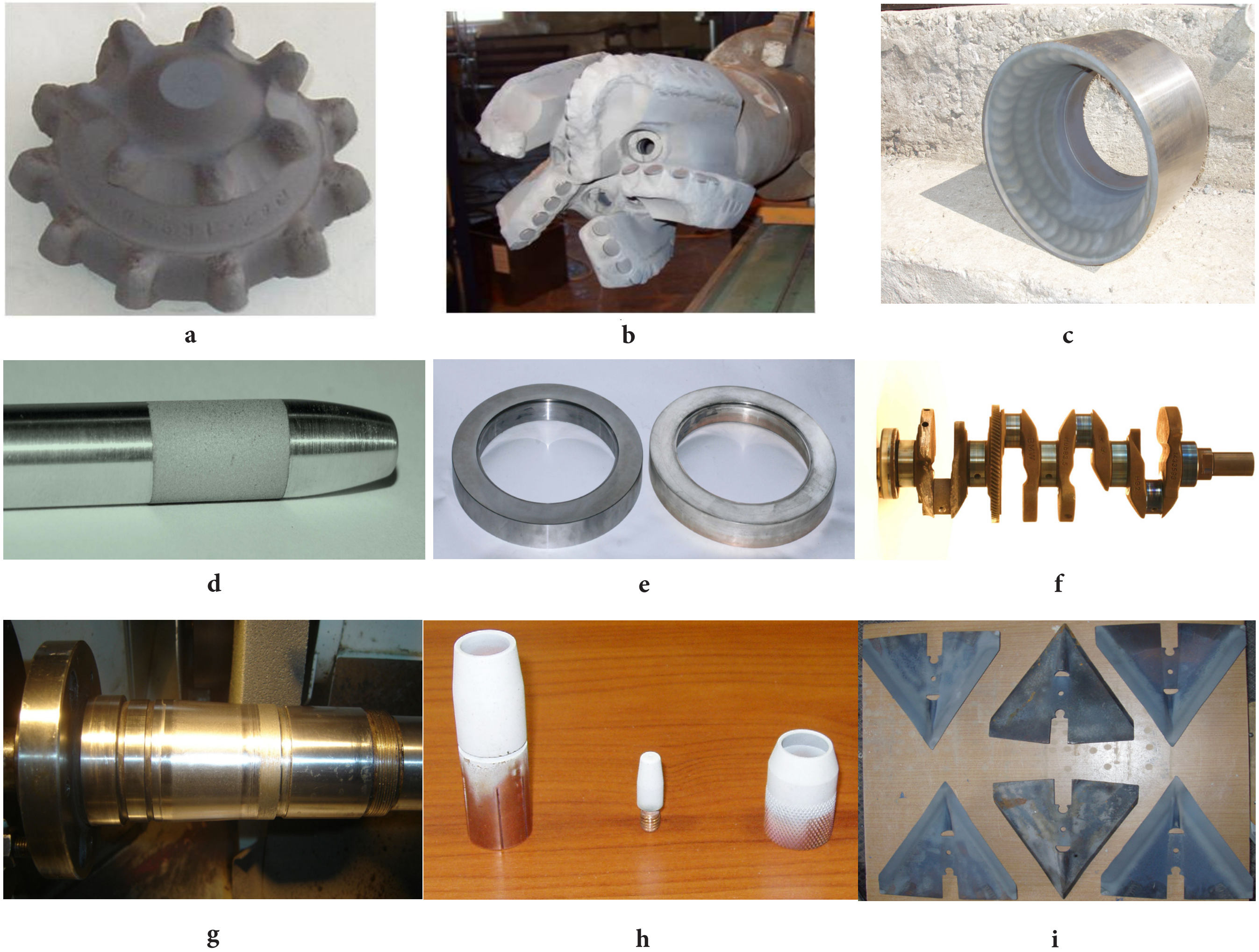

Figure 6. Applications of detonation coatings.

The above list of applications of detonation coatings is not exhaustive. The circle of treated parts has been constantly expanding and detonation sputtering techniques and equipment have been constantly improving, thus opening new perspectives and applications of this technology:

–Reinforcing parts, accessories and tools that are prone to excessive wear (drilling tools; vanes and other parts of aviation engines; end shaft seals; knifes and cutters for plastics, leather, wood, asbestos cement boards; medical and measuring tools; welding drive rollers; die molts etc.);

–Reconstructive maintenance of parts and accessories;

–Applying special coatings: corrosion resistant, electroinsulating, friction, anti-friction, heat resistance, electroconductive and other coatings that have special properties.

4. Conclusions

Our research showed that the suggested technology ensures higher stability of mechanical properties of coatings. Thus, original hardness of steel specimens was in the range of 400 to 600 kgf/mm^2. Hardness values of detonation-sputtered hard-alloy coatings were ca. 1,200 to 1,400 kgf/mm^2 and activation energy was up to 350 kJ/mole, which is typical of hard-alloy materials. Scratch-hardness tests showed rather high coating and base material adhesion values. Deformation of the transitory zone by a diamond indenter did not lead to any peeling or shearing of the coating in any case, which is indicative of possible further processing (grinding) of coated surfaces.

5. Acknowledgement

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