Powder Metallurgy and Metal Ceramics, Vol. 47, Nos. 1-2, 2008

CONTROLLING THE PROPERTIES OF DETONATION-SPRAYED COATINGS: MAJOR ASPECTS

E. A. Astakhov

UDC 621.762

A system approach to controlling the quality of detonation-sprayed coatings is developed. It includes such stages as selecting powder characteristics and gas composition, forming a gas-powder mixture, adjusting the parameters of two-phase pulse flow, and ensuring contact interaction needed to form the coating that depends on the material and preset service properties of the layer sprayed.

Keywords: *coating, detonation-sprayed coating, particle velocity and temperature, layer formation, properties of coatings.*

Modern engineering, the reliability and life of machines and mechanisms, and the performance of equipment considerably depend on the development and application of various protective coatings. They impart products with a unique combination of properties that cannot be achieved with traditional structural materials.

One of the promising methods of protection against wear and hot corrosion in power engineering, aircraft, motor-car, and turbine construction, petrochemistry, and metallurgy is detonation spraying (DS). Its advantages are high bonding strength (100–180 MPa) between the coating and substrate, high density of the protective layer (porosity less than 1%), and the possibility of spraying almost any material on any substrate without change in the properties of the base material. The high performance of detonation coatings makes it possible to extend considerably (five- to ten-fold or, in some cases, by a factor of 20 to 30) the life of units and mechanisms.

Research on detonation spraying was initiated by Grigorii Samsonov at the Institute for Problems of Materials Science, Academy of Sciences of the Ukrainian SSR, in the early sixties. In 1972, he also initiated continuation of the research at the Leninskaya Kuznitsa Central Design Bureau, which puts scientific achievements into practice at shipbuilding plants [1–4].

This paper is dedicated to the memory of Grigorii Samsonov, a great scientist and teacher.

The time is now ripe to generalize and analyze the accumulated theoretical and experimental data to lay the scientific foundation of the DS process, which would allow controlling the properties of coatings, and to develop technologies and industrial equipment for spraying coatings of various purposes. The modern theory of thermal-sprayed coatings is based on the studies initiated by M. Kh. Shorshorov, V. V. Kudinov, Yu. A. Kharlamov under the guidance of academician N. I. Rykalin and continued by V. I. Pokhmurskii, Yu. S. Borisov, I. L. Kupriyanov, and E. A. Astakhov at the A. A. Baikov Institute of Metallurgy.

An analysis of the results from the studies shows that besides a number of common features associated with the nature of the process and material (lamination, discreteness, inhomogeneity of coatings, presence of pores and oxide inclusions, various boundaries), thermal-sprayed coatings obtained by different methods also show significant differences associated with technological features of the process. Among them are differences in the degree of oxidation of the sprayed material, in the phase composition and properties of the coating, and in the changes of the mechanical properties of the substrate. In this context, it is clear why there is a tendency to develop spraying processes that would use supersonic gas jets (detonation, supersonic plasma, and supersonic gas-flame methods) to increase the kinetic energy of particles of the sprayed material and, thus, to improve the formation conditions for and the properties of the protective coating.

Electric Welding Institute, National Academy of Sciences of Ukraine. Translated from Poroshkovaya Metallurgiya, Vol. 47, No. 1–2 (459), pp. 91–104, 2008. Original article submitted December 1, 2007.

Most such studies address the properties of sprayed coatings without discussion of their dependence on the process conditions. Moreover, experimental studies intended to evaluate the effect of various factors on the structure and properties of coatings are few and are not integrated, i.e., they address only one or several factors. Therefore, the need arises to develop a system approach to controlling the DS process and the properties of coatings depending on the type of material, and to provide high performance of systems of the spraying machine in pulse mode (up to 10 Hz) [5].

A new detonation spraying method (patented in the USA, Germany, Japan, France, and Switzerland) that provides more homogeneous detonation mixture was proposed. It differs from the traditional method by continuous feed (stationary gas flow) of a mixture of combustible gases (for example, oxygen and acetylene) to the combustion chamber. The process is made periodic and the gas mixture is kept away from the detonation products (DPs) by feeding a neutral gas (nitrogen, argon) between supply of powder and ignition of the gas mixture. Since the pressure of nitrogen is 2.5 to 3.0 times higher than the pressure of combustible gases, they are blocked. The mixing of gases in the mixture preparation and protection unit makes three-component mixtures more uniform, and the larger surface of the porous filter reduces the hydraulic resistance of the gas piping.

The gas-distribution switching unit simplifies the feed of the sprayed powder and gas mixture and its ignition in the combustion chamber and increases the firing rate to 6 Hz. Each pipe is equipped with high-precision pressure differential controllers, which made it possible to stabilize the output parameters of gas flows and produce coatings with stably high performance characteristics.

The major aspect in the formation of the gas-mixture–powder system is the way the powder is fed into the barrel. Devices for lateral and axial feed of the powder in pulse and continuous modes were developed in [6, 7]. In the pulse lateral feed mode, the powder is introduced into the appropriate zone of the barrel and at the appropriate time owing to the use of a cyclogram.

However, the direction of powder feed is not aligned with the direction of its accelerated motion, which leads to sticking and clustering of particles to the barrel walls and requires additional measures to level the concentration across the cross-section and length of the barrel. This shortcoming is eliminated in the axial continuous feed mode, which provides uniform concentration across the length and cross-section of the barrel [8]. However, the charge of powder expands into a long plume along the barrel so that the optimal conditions for coating are only achieved in the central region of the powder flow. As consequence, the properties of the layer change across its thickness. The pulse axial feed mode prevents the powder from being at the beginning and the end of the barrel and levels the properties of the coating across its thickness.

To determine the amount of powder, extent, and the location of the powder cloud in the barrel at the time of ignition, a specially developed device is used to control the powder in detonation products. Its operation principle is that the detected (by a photosensor) intensity of light from DPs increases if they contain heated powder particles.

Calculation and experimental determination of gas-dynamic parameters made it possible to establish the dependence of the temperature and the acceleration of powder particles on the process parameters [5].

Calculations conducted using the laws of conservation of mass and momentum and the Jouget conditions (the detonation velocity is equal to the sum of the velocities of burnt gas and sound in it) indicate the possibility of using propane–butane–oxygen mixtures for DPs instead of acetylene–oxygen. As regards the dynamic effect on powder particles, propane–oxygen mixtures are preferred because their dynamic head is 20–25% higher.

Measurements of the velocity of powder particles suggest that change in the position of the powder cloud in the barrel at the time of ignition by increasing the delay time from 50 to 200 sec increases the velocity of the major portion of the powder from 300 to 750–1000 km/sec, while increase in the oxygen content of the gas mixture as well as addition of nitrogen reduces the velocity of particles [5]. Decrease in the oxygen content of the acetylene–oxygen mixture and addition of nitrogen increases the spraying distance, while the filling of the barrel above 50 % decreases the temperature of powder particles.

Table 1 presents the velocity and temperature of particles in different spraying conditions.

The system approach to controlling the conditions for the formation of detonation coatings is based on theoretical and experimental data on the deformation of particles upon impact, physical contact, and optimal surface microrelief; the parameters of the thermal cycle between a particle and the substrate in DC; the major factors affecting the kinetics and mechanism of interaction of particles with the substrate and with each other; dependence of the process parameters on the characteristic of the material sprayed.

The discreteness of the DS process allows us to systematize and group the factors that are decisive at different stages of the process [9]. There are three major stages in the detonation spraying process. The first stage — preparatory — involves filling of the barrel with an explosive mixture and a powder to be sprayed. This stage ends at the time of initiation of detonation. At the second stage, the thermal and kinetic energy of detonation products is imparted to the powder particles during motion between the surface being coated and muzzle. The third stage is the formation of a detonation coating on the substrate.

The decisive factors of the first stage are the composition of the gas mixture, degree of filling of the barrel, powder charge, particle sizes, particle shapes, position and concentration of the powder cloud in the barrel at the time of detonation initiation, and the distance from the muzzle to the substrate. These are process parameters. Of no less importance are design features and parameters of the spraying machine itself: the size and shape of the barrel, the place where the mixture is ignited, methods of transfer and the place of feeding the powder into the barrel, firing rate.

TABLE 1. Velocity and Temperature of Sprayed Particles Depending on Process Conditions

Sprayed material	Particle size, μm	Velocity, m/sec	Temperature, °C
$C_3H_8 + 3.5\ O_2$, barrel length 1200 mm*			
Ni	<10	1350	1400
Ni	20–40	1200	1200
Ni	4–63	1050	1000
Ni	63–80	800	650
WC + Co	1–3	1300	1400
WC + Co	63–80	1000	950
$C_2H_2 + O_2$, barrel length 1200 mm			
Ni	<10	1300	1450
Ni	2–40	1150	1300
Ni	4–63	1000	1250
Ni	63–80	750	1100
WC + Co	1–3	1250	1450
WC + Co	20–40	1050	1200
$C_3H_8 + 3.5\ O_2$, barrel length 550 mm			
Ni	<10	1250	1350
Ni	20–40	1000	1200
Ni	40–63	750	1050
Ni	63–80	300	750
WC + Co	1–3	1200	1350
WC + Co	20–40	700	1000
$C_2H_2 + 2.5\ O_2$, barrel length 1200 mm			
Al_2O_3	2–5	450	2200
Al_2O_3	10–20	300	2000
$C_3H_8 + 7.0\ O_2$, barrel length 1200 mm			
Al_2O_3	2–5	500	2050
Al_2O_3	10–20	400	1800

* Barrel diameter is 20 mm in all cases.

The decisive factors of the second stage are the energy characteristics (their temperature and velocity) of DPs and powder particles, the pressure and density of the gas, and the period during which the powder is in the high-temperature flow. At the third stage, the decisive factors are those on which the number of bonds formed between the interacting materials at the coating–substrate interface depends. Among such factors are the temperature and pressure in the zone of physical and chemical processes between the contacting materials and the duration of these processes.

Apart from the above factors, the physical characteristics of the coating material play an important role at all stages of the process and the characteristics of the substrate material at the third stage.

If a two-phase flow exists no longer than $5 \cdot 10^{-3}$ sec during DS and the optimal powder charge is 0.25 g, one can justifiably assume that each particle deforms and hardens individually. The independent behavior of particles on the substrate significantly facilitates the analysis of the coating formation process: it just remains to examine the thermal, physical, and chemical phenomena accompanying impact and deformation.

For DS it is typical when both a particle and the substrate deform upon impact. At the time of collision (at velocities of 500–1000 km/sec) the substrate undergoes continuous plastic deformation. Changes in the surface microrelief of a titanium substrate during coating with nickel were observed in [10].

An analysis of profilograms reveals surface damages of two types: a microroughness and waviness. The maximum size of microroughnesses (~1.4 μm) is an order magnitude less than the size of sprayed particles. This may be regarded as evidence of the joint plastic deformation of particles and substrate accompanied by wave formation on the contact surface. Waviness occurs only where coating is already present. The pitch of waves is approximately 8.5 mm and the wave height is 6.2 μm. The maximum height of microroughnesses (and, thus, the amplitude and length of waves) was observed at a distance of 8–10 mm from the barrel axis, which means that at a spraying distance of 150 mm, separate particles (started moving along the barrel axis) can be incident on the surface being coated at an angle of 4°.

The intensity of plastic deformation of sprayed particles during the formation of a protective WC–Co layer was determined in [11] in analyzing the conductivity of the coating. The electrical resistivity ($\Omega \cdot \mathrm{m} \cdot 10^{-7}$) is 1.8 after spraying and 4.5 after annealing in the perpendicular direction to the spraying axis and 6.7 after spraying and 7.5 after annealing in the parallel direction to the spraying axis. The anisotropic electrical resistivity of the coating layer is used to estimate the coefficient of deformation ω of particles. Expressing the coefficient of deformation in terms of the ratio of the resistivities in the parallel and perpendicular directions, we obtain $10 < \omega < 10^2$ for WC–Co coating and $10^2 < \omega < 10^3$ for Al_2O_3 coating, which is indicative of different heating conditions for WC–Co and Al_2O_3 coatings.

Upon impact against the substrate, the kinetic energy of particles forces them to deform intensively and generates pressure in the contact region. In hydrodynamics, two components of such pressure are considered: shock and head. The shock pressure P_{sh} generated at the initial moment of impact in the contact region between a particle and the substrate is determined from the following equation [12]:

$$P_{\mathrm{sh}} = \frac{1}{1 + \frac{\rho_{\mathrm{p}} C_{\mathrm{p}}}{\rho_{\mathrm{sb}} C_{\mathrm{sb}}}} \rho_{\mathrm{p}} C_{\mathrm{p}} U_{\mathrm{p}}, \tag{1}$$

where ρ_{p} and ρ_{sb} are the densities of particles and substrate; C_{p} and C_{sb} are the speeds of sound in the materials of particles and substrate; and U_{p} is the velocity of particles.

At the instant a drop spreads, the pressure in the contact region instantaneously drops to the level of pressure head, which is determined by the following equation in the elementary case (the substrate is perfectly rigid and the melt is perfectly liquid) [13]:

$$P_{\mathrm{h}} = \rho_{\mathrm{p}} \cdot U_{\mathrm{p}}^2. \tag{2}$$

The calculation of pressures by formulas (1) and (2) in the contact region between particles of Ni and W and substrate of W, Fe, Cu, Ni, Ti, and Al and the estimation of the duration of their action allow us to draw the following conclusions. In the range of velocities from 400 to 1000 km/sec, the shock pressure changes from 10 to 50 GN/m^2 and the pressure head from 5 to 15 GN/m^2. Increase in the velocity of sprayed particles decreases the difference between the shock pressure and the pressure head. The higher the density of the material of particles, the more significant this decrease. The pressure head acts approximately an order of magnitude longer than the shock pressure does, and the area affected by the pressure head is several orders of magnitude larger than that acted upon by the shock pressure.

The contact temperature can be calculated by the Veinik formula [14]:

$$T_{\mathrm{c}} = \frac{B_{\mathrm{p}} T_{\mathrm{p}} + B_{\mathrm{sb}} T_{\mathrm{sb}}}{B_{\mathrm{p}} + B_{\mathrm{sb}}}, \qquad (3)$$

where $B = \sqrt{\lambda c \rho}$ is the heat storage coefficient (λ is the thermal conductivity, c is the thermal capacity, and ρ is the density).

An analysis of the thermal cycle reveals that the contact region is heated and cooled during DS in 10^{-7} to 10^{-10} sec, which is two to five orders of magnitude less than the collision frequency [5].

At the final stage of the coating process, bonds among surface atoms form, resulting from quantum processes of electronic interaction. For these processes to take place, additional energy is required. It is the thermal and kinetic energy of the sprayed particles.

To study the laws governing the formation of the structure and properties of detonation coatings, which depend on the production process for and the properties of powders and, on the one hand, on the DS process conditions, on the other hand, we selected materials from three different groups with different spraying conditions and differing methods to control the properties of coatings. The first group includes materials that become plastic at temperatures below the melting point. Among such materials are metals (Al, Ti, Fe), alloys (Al–Cu–Fe, Ni–Al), and mechanical mixtures or composite powders with a plastic component (WC–Co, TiC–Ni, WC–Ni, Cr_3C_2–Ni, etc.). The properties of coatings made of such materials are controlled by providing spraying conditions under which the powder particles of the low-melting component are heated up to 0.8–0.9 T_{pl} and are accelerated to a velocity maximum possible for the detonation process. Coating quality criteria are bond strength with the substrate, the density and hardness of the coating layer, and preserved chemical and phase composition of the original material.

Of special interest for engineering are coatings that have a refractory component (carbides, borides, etc.) and metal bond (Ni, Co, Fe) with low melting point. A typical representative is VK15 alloy (WC–15% Co) as the most effective protection against wear at low temperatures (to 570°C) and under high dynamic loads [15, 16]. In spraying of WC–Co powders with 1–4 μm particles, their phase composition undergoes consecutive transformations $WC \rightarrow W_2C \rightarrow W$ accompanied by the formation of the carbides Co_3W_3C and $Co_3W_9C_4$ and the intermetallic compound Co_7W_6. These transformations occur both in the barrel and on the substrate during the formation of the coating layer.

A metallographic analysis shows that coatings are a low-porous layer tightly bonded to the substrate. Carbides, cobalt, and η-phase are uniformly distributed over the volume of the coating, without coagulation, resulting in stable microhardness that depends only on the spraying conditions and varies between 10000 and 12000 MPa. The reduction in the microhardness of the coating layer with increase in the oxygen content of the mixture is indicative of the decarbonization of the sprayed material, which is confirmed by chemical and X-ray phase analyses. The maximum bond strength is achieved with a 1.2 : 1.0 mixture of oxygen and acetylene and a 3.5 : 1 mixture of propane and butane. Adding 30% of nitrogen enhances the strength and quality of the layer.

As the size of particles (>20 μm) increases, the strength of the coating reduces and the porosity and pore size increase (by no more than 1–1.5%). A metallographic analysis reveals the phase heterogeneity of the coating. Microhardness varies from 12000 to 8000 MPa. An X-ray phase analysis shows that along with WC and cobalt there is W_2C and brittle η-phase formed along the boundaries of WC–Co.

The structure and microrelief of the coatings obtained with axially fed powder manifest significant advantage: no conglomerated particles, uniform distribution of particles, and, consequently, low roughness of the surface.

The behavior of detonation carbide coatings in friction units was studied in [17]. The wear resistance of a VK15 coating layer in homogeneous water-lubricated friction pair is higher by a factor of 50 to 150 than in a homogeneous oxidized-titanium pair, while the dynamic coefficient of friction is lower by a factor of 1.5 to 2.0.

The wear resistance of a homogeneous VK15-coating pair is almost 10-fold higher than that of a heterogeneous pair made of oxidized VT5 alloy and bronze. The dynamic coefficients of friction of both materials are similar.

The second group includes plastic materials that should be heated to the melting point to form hardened structures. Among such materials are amorphized alloys, when their melts are cooled at rates no less than 10^5 K/sec, amorphous or fine-crystalline structures form. The properties of such coatings can be controlled by changing the thickness of the layer in a cycle. The less the thickness of the layer, the higher the velocity and temperatures of particles. A coating quality criterion is the amount of the amorphous phase formed.

The process factors important for the formation of amorphous coatings were identified in [18, 19]. Such factors (Table 2) are the ratio of the volume flow rates of fuel and oxidizer in the detonation mixture, which determine the temperature, velocity, and chemical composition of DPs (modes 1 and 2); the amount of neutral gas added to the detonation mixture to change the velocity and temperature of sprayed particles and the degree of their chemical interaction with DPs (modes 1 and 3); the fraction of the sprayed material, which determined the thickness of hardening particles and, hence, their cooling rate (modes 1, 5, and 6); the ratio of the volume of the detonation mixture and the amount of the sprayed material, which is most significant for the thermal processes in the two-phase flow, including heating of the sprayed material (modes 4 and 5).

It was established that as the power of chemical activity of the detonation mixture decreases with increase in the velocity of DPs, the fraction of the amorphous phase increases and the gas content of the coating decreases (Table 2). Increase in the volume of the detonation mixture at constant flow rate of the sprayed material also leads to decrease in porosity and increase in hardness (modes 1 and 3). If the amount of acetylene and oxygen in the detonation mixture is proportionally decreased (modes 4 and 5), the velocity of DPs decreases and the DPs longer interact with the sprayed material, which deteriorates the quality of the coating in all controllable characteristics.

As the particle size increases, the amount of nonfused particles with hereditary structure in the coating increases, raising its porosity and decreasing the fraction of the amorphous phase. Increase in the velocity of DPs improves the quality of coatings, i.e., decreases the porosity and increases the microhardness and amount of the amorphous phase.

Tribotechnical tests with back and forth motion established that the wear resistance of amorphized coatings based on iron and nickel alloys in mixed and dry friction units is much higher than that of structural and tool steels after thermal and thermochemical treatment and, in some cases, that of WC–Co coatings. For example, when subjected to dry friction and lubricated friction in an end friction machine, Ni–Cr–Fe–B–Si–C coatings with mainly amorphous structure show less linear wear by a factor of 1.8 to 3.2 than 20X case-hardened steel does.

Spraying modes that increase the volume fraction of the amorphous phase in $Fe_{40}Ni_{40}B_{20}$ coating improve their tribotechnical characteristics. Amsler tests made it possible to reveal the high wear resistance of steel 45 with sprayed amorphized Fe–Ni–B and Ni–Cr–Fe–B–Si–C coatings. Amorphous coatings increase the endurance limit of the substrate. For example, tests on structural-steel samples with amorphous Ni–Fe–Cr–B–Ni–C, Fe–Ni–B, Ni–Cr–Mo–B, and Fe–Cr–Mo–B coatings subjected to twisting and bending on a PUNN-type Schenck fatigue testing machine (load frequency 100 Hz; number of cycles 10^7) showed that the coating increases the endurance limit by 25–45% on the average compared with steel without coating.

TABLE 2. Detonation Spraying Modes for $Fe_{40}Ni_{40}B_{20}$ Coatings and Their Properties

Spraying mode	Particle size, μm	Gas flow rate			Amount of amorphous phase, %	Amount of dissolved gases		Hardness, MPa	Bond strength, MPa
		C_2H_2	O_2	N_2		$[O_2]$	$[N_2]$		
1	5–40	0.5	0.5	0.5	70	0.24	0.53	720	58
2	5–40	0.5	1.5	0.5	40	1.6	3.6	645	54
3	5–40	1.0	1.0	1.0	80	0.29	0.78	810	70
4	50–63	1.0	1.0	0.5	70	0.81	1.5	780	59
5	50–63	0.5	0.5	0.5	65	0.19	0.38	750	54
6	100–160	0.5	0.5	0.5	40	0.15	0.31	630	45

It was established that amorphization considerably enhances the corrosion resistance of alloys. For example, the corrosion current density of amorphous $Fe_{77}P_{18}C_5$ coatings in 10% solution of hydrogen peroxide is $0.09 \cdot 10^{-4}$ mA/m^2 versus 10^{-4} mA/m^2 in the original crystalline alloy. The corrosion resistance of amorphous Fe–Cr–P–C coatings is 10-fold higher than that of nickel-chromium stainless steels.

To produce a coating with high content of amorphous phase, it is necessary to vary process parameters so as to heat the sprayed particles to the melting point (which determines the composition of the detonation mixture) and then to cool them at a rate of 10^5–10^7 K/sec (which determines the size of sprayed particles and the degree of their deformation). There are heat treatment conditions under which amorphous coatings have nanostructures 100 nm in size.

The third group includes nonplastic materials that are capable of forming coatings from melt only. These materials are mainly oxides. In aluminum oxide spraying during which polymorphic transformations occur, the properties of the coating can be controlled by changing its thickness in a cycle. A quality criterion is the amount of the α-Al_2O_3 phase, which has maximum hardness. It can become higher by increasing the thickness of the sprayed layer in a cycle to decreasing the rate of cooling of the melt. The aluminum-oxide spraying process is distinguished by the significant difference between the conditions of formation of the initial coating on the substrate and of the subsequent coating layers.

It was established that the properties of oxide coatings are directly dependent on the temperature of particles during the formation of the coating. The maximum bond strength (40–45 MPa) is achieved when the particles are heated to the melting point. The layer contacting with the substrate contains a metastable γ-phase that is more chemically active than the α-phase, which is important for the contact interaction with the oxide film on the surface of the substrate. The γ-phase forms more intensively when the melt is quenched. To increase the content of the α-phase in the subsequent layers so as to enhance their wear resistance by a factor of 3 to 5, it is necessary to decrease the rate of cooling of the melt by increasing the thickness of the subsequent layers in a cycle by a factor of 1.5 to 2.0 [20].

The antifrictional properties of Al_2O_3 coatings have been studied. In a homogeneous friction pair subjected to a specific load of 5 MPa, aluminum oxide prevented the friction surfaces from damage on a slip distance of 5 km; the wear was 0.8 μm for the ring and 8.9 μm for the pin; the coefficient of friction was 0.346–0.486. The coefficient of friction in a friction pair with dissimilar components (Al_2O_3–BrOF 10-1 bronze) in water with AMS-1 grease was 0.092–0.162. An analysis shows that for two years the wear of the BrOF 10-1 bronze bearing of the rudder head may reach 0.5 mm and the wear of the coating layer 25 μm.

Electrochemical measurements (plotting of polarizing curves, measurement of stationary potentials and potentials of contact pairs) and general, contact, and crevice corrosion tests showed high corrosion resistance of Al_2O_3 coatings on samples made of 0Kh18N10T steel, 3M titanium alloy, and steel 45 with a coating layer impregnated with Anaterm-1 anaerobic hermetic.

The effect of VK15 and Al_2O_3 coatings (0.2–0.3 mm thick) on the short-term strength, plasticity, impact strength, and endurance limit of steel 45, stainless steel, and 3V and 3M titanium alloys was examined in [21]. The 3V alloy and stainless steel samples with VK15 coating showed decrease in strength and relative elongation, while the impact strength of the 3V alloy increased insignificantly. The Al_2O_3 coating on steel 45 has a very weak effect on the strength and plastic properties of the base metal. The ultimate strength and yield stress of OKh18N10T steel samples increased insignificantly. The Al_2O_3 coating slightly changed (by less than 7%) the impact strength of steel 45, 3M alloy, and OKh18N10T stainless steel. The endurance limit of titanium alloys decreased 35–37%, irrespective of the material of the coating, whereas the endurance limit of OKh18N10T steel depends on the material of the coating: it decreases by 40% with VK15 coating and by 47% with Al_2O_3 coating.

CONCLUSIONS

The process conditions for producing detonation coatings with high adhesive and cohesive strength (to 180 MPa), low porosity (0.2–1.0%), and high physical, mechanical, and performance properties from various classes of powder materials have been scientifically justified and experimentally tested. An analysis of these conditions has revealed that because of the main difference of detonation spraying from plasma and gas-flame spraying (high velocity

(400–1250 km/sec) and, hence, high kinetic energy of sprayed particles), the pressure head generated in forming the protective layer reaches levels used in dynamic hot-pressing (5–15 GN/m^2). This makes it possible to spray particles of a material heated to a highly plastic state, without the need to melt it. In this connection, materials used for DS are classed into two groups differing by the temperature to which particles should be heated. The first group includes metals, alloys, and cermets with metallic bond (for example, WC–Co), which can be used for coating at temperatures of 0.8–0.9 T_{melt} and accelerations of 400–1250 km/sec. This makes it possible to reduce the adverse effect of high temperatures (degradation, oxidation, etc.). The second group includes oxides, oxygen-free refractory compounds, and alloys that form coatings with metastable structure (amorphized, quasicrystalline, etc.), when hardened after being melted, i.e., their particles should be melted.

A system approach has been developed to control the quality of detonation-sprayed coatings, including the following stages: selecting the characteristics of the powder and composition of the gas mixture; forming the gas–powder mixture; adjusting the parameters of the impulsive two-phase flow; ensuring the necessary contact conditions related to the type of the sprayed material and the prescribed performance properties of the protective layer.

The gas-dynamic parameters of detonating gas mixtures have been assessed; the concentration ratios of the components of detonation mixtures that provide a stable detonation process in the gun barrel have been found; the influence of these ratios on the energy parameters of sprayed particles has been studied when spraying machines operate in automatic mode. The replacement of acetylene by propane–butane mixture has been justified. It was experimentally shown that this replacement does not deteriorate the quality of sprayed coatings and enhances the safety of the spraying process.

The interaction of accelerated heated powder particles with the substrate has been studied. It was shown that if the velocity changes from 400 to 1000 km/sec, the shock pressure changes from 10 to 50 GN/m^2 and the pressure head from 5 to 15 GN/m^2.

Increasing the velocity of sprayed particles reduces the difference between the shock pressure and the pressure head; the higher the density of the material of particles, the less this difference. An assessment of the thermal cycle in the contact region shows that it is heated and cooled in 10^{-7}–10^{-10} sec, which two to five orders of magnitude less than the collision frequency.

It was experimentally proved that the structure and properties of WC–Co coatings depend equally on the process parameters (composition of the detonation mixture, the size of sprayed particles, charge per cycle, the length of the barrel, and the location of the powder in the barrel) and on the method of preparation of the initial material (mechanical mixture, sintered and ground powder, conglomerated, coated etc.). The influence of the method to feed the powder (lateral, axial, impulsive, continuous) on the stable density distribution of the gas–powder mixture along the barrel has been studied. It has been established that the maximum bond strength can be achieved with acetylene and oxidizer in the ratio 1.2 : 1.0 and with 3.5 : 1.0 propane–butane mixture. Adding 30% of nitrogen improves the quality of coatings due to reduced thermal effect on WC–Co powder.

An analysis of theoretical and experimental data on the deformation of sprayed particles in creating coatings with amorphous or microcrystalline structure has revealed the following. First, the strain rate of the sprayed particle on the substrate is at least ten-fold higher than the rate of hardening, i.e., an individual structural fragment of coating of a deformed particle forms prior to its hardening. Second, the thickness of deformed particles allows predicting high rates of cooling (10^5–10^7 K/sec) exceeding the critical values at which melt transforms into an amorphous state for the majority amorphized alloys. Third, the bond strength of coatings on the substrate, the endurance limit of the substrate, wear and corrosion resistance of coatings depend on the volume fraction of the amorphous phase.

The necessary condition for the amorphization of metal alloys in DS has been formulated, and rational spraying modes (for the Fe–B system as an example) with the use of various gases that provide the volume fraction of the amorphous phase between 50 and 80% have been identified. It is shown for the first time that mainly residual compressive stresses are induced in amorphized coatings; they increase as the substrate is heated during spraying. The residual compressive stresses increase the endurance limit of the substrate by 10–30%.

It has been established that the properties of oxide coatings are directly dependent on the temperature of particles during the formation of the coating layer. The maximum bond strength (40–45 MPa) is achieved when particles are heated to the melting point. In this case, the protective layer has a metastable γ-phase that is more chemically active than the α-phase, which is important for the contact interaction with the oxide film on the surface of the substrate. The γ-phase forms more intensively when the melt is quenched. To increase the content of the α-phase in the subsequent layers so as to enhance their wear resistance by a factor of 3 to 5, it is necessary to decrease the rate of cooling of the melt by increasing the thickness of layers in a cycle by a factor of 1.5 to 2.

The dependence of the mechanical properties, corrosion resistance, structural strength, and wear resistance of the coating on the process parameters has been examined. It has been established that Al_2O_3 coatings on titanium alloy, steel 45, and OKh18N10T steel have a very weak effect on the strength and plastic properties of the substrate, but reduce the endurance limit by 35% for titanium alloy and by 40% for stainless steel.

A new detonation spraying method has been proposed. It continuously (stationary gas flow) feeds the gas mixture into the combustion chamber and makes the process cyclic by periodically supplying neutral gas under high pressure between powder feeding and mixture ignition.

REFERENCES

1. V. I. Shesternenkov, *Detonation Spraying of Coatings* [in Russian], Author's Abstract of PhD Thesis, Inst. Probl. Materialoved. AN USSR, Kiev (1969), p. 22.
2. E. A. Astakhov, *Studying of Detonation Spraying of Coatings and Their Properties* [in Russian], Author's Abstract of PhD Thesis, Inst. Probl. Materialoved. AN USSR, Kiev (1973), p. 29.
3. G. V. Samsonov, S. Yu, Sharivker, E. A. Astakhov, and A. P. Garda, "Some features of detonation spraying of coatings," in: *Inorganic and Organic Coatings* [in Russian], Nauka, Leningrad (1975), pp. 80–86.
4. G. V. Samsonov, B. N. Dvukraev, S. Yu. Sharivker, et al., *A Detonation Coating Machine* [in Russian], Inventor's Certificate No. 513728 USSR, Okryt. Izobret., No. 8 (1976).
5. A. I. Zverev, S. Yu. Sharivker, and E. A. Astakhov, *Detonation Spraying of Coatings* [in Russian], Sudostroenie, Leningrad (1979), p. 232.
6. E. A. Astakhov, A. I. Zverev, S. Yu. Sharivker, and V. I. Pashchenko, "Metering devices for detonation spray deposition," *Powder Metall. Met. Ceram.*, 18, No. 3, 203–206 (1979).
7. E. A. Astakhov, A. I. Zverev, S. Yu. Sharivker, et al., "Characteristics of two methods of powder introduction in detonation spray-deposition," *Powder Metall. Met. Ceram.*, **17**, No. 1, 82–85 (1978).
8. E. A. Astakhov, "Perun-S detonation coating system," *Autom. Svarka*, No. 2, 38–43 (2003).
9. E. A. Astakhov and V. S. Klimenko, *Technology to Restore and Harden Workpieces with Detonation Coatings* [in Russian], Znanie, Kiev (1981), p. 20.
10. S. Yu. Sharivker, Ts. A, Kanevskii, E. A. Astakhov, and K. D. Modylevskaya, "Surface relief on the basis metal in detonation spray deposition," *Powder Metall. Met. Ceram.*, **15**, No. 2, 157–158 (1976).
11. Ts. A. Kanevskii, S. Yu. Sharivker, A. P. Garda, et al., "Electrical conductivity of detonation-deposited hard-alloy coatings," *Powder Metall. Met. Ceram.*, **14**, No. 12, 1029–1032 (1975).
12. M. Kh. Shorshorov, et al., "Mechanism and kinetics of formation of protective coatings in detonation spraying," in: *Protective Coatings on Metals* [in Russian], Issue 10, Naukova Dumka, Kiev (1975), p. 126.
13. S. V. Petrov and I. N. Karp, *Plasma Air–Gas Spraying* [in Russian], Naukova Dumka, Kiev (1993), p. 194.
14. A. I. Veinik, *Theory of Alloy Hardening* [in Russian], Mashgiz, Moscow (1960), p. 180.
15. K. A. Yushchenko, E. A. Astakhov, V. S. Klimenko, and Yu. S. Borisov, "Detonation spraying of strengthening coatings and its development," in: *New Processes and Equipment for Thermal-Spray and Vacuum Coating* [in Russian], Inst. Élektosvarki NAN Ukrainy, Kiev (1990), pp. 26–32.
16. Yu. G. Tkachenko, V. V. Sychev, L. M. Apininskaya et al., "Wear resistant hard-alloy coatings," *Powder Metall. Met. Ceram.*, **14**, No. 5, 552–554 (1975).
17. V. N. Gol'dfain, E. A. Astakhov, A. I. Zverev, and V. P. Lukina, "Antifriction properties of a VK15 alloy coating applied by the detonation method to VT5 alloy," *Powder Metall. Met. Ceram.*, **18**, No. 1, 63–66 (1979).
18. E. A. Astakhov, V. N. Korzhik, and A. V. Chernyshev, *Detonation Spraying of Amorphous and Microcrystalline Coatings* [in Russian], Znanie, Kiev (1990), p. 20.

19. Yu. S. Borisov, V. E. Oliker, E. A. Astakhov, et al., "Structure and properties of gas-thermal coatings of Fe–B–C and Fe–Ti–B–C alloys," *Powder Metall. Met. Ceram.*, **26**, No. 4, 313–318 (1987).
20. E. A. Astakhov, "Antifriction properties and corrosion resistance of Al_2O_3 detonation coating applied in ship mechanical engineering," *Automat. Svarka*, No. 11, 20–22 (2004).
21. E. A. Astakhov, "Influence of detonation coatings on the mechanical properties of products," *Automat. Svarka*, No. 6, 56–57 (2004).