NOVEL ANTICORROSIVE COATING FOR RUST PROTECTION OF STRUCTURES

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Abstract

The coating is intended for rust protection of ferrous metal structures operating in slightly and highly aggressive environments, such as ship hulls, off-shore oil platforms and pipelines. The composite coating contains an aluminium matrix with a uniformly distributed and metallurgically bonded ceramic particles, has low porosity of 0.5 %, good adhesion to the substrate and tensile strength of 35 MPa. The coating is produced by high-energy plasma spraying. Its thickness ranges from 0.2 to 0.3 mm. The coating is characterized by a high corrosion resistance in an aggressive environment with pH equal to 2-12 and in salt solutions. The aluminoceramic coating does not change its initial properties and plays the protective role under the effect of main operational aging factors, such as temperature, combined effect of temperature and humidity, corrosive environment and electric potentials.

Introduction

Typical corrosion-resistant coatings intended for protection of ferrous metal structures and constructions include aluminium, aluminozinc and zinc thermal spray coatings. They compete with paint-and-varnish and galvanic coatings, melt dip coatings, vitreous-enamel, bitumen, bitumen-rubber, polymeric and epoxy coatings. As compared with zinc or aluminozinc coatings, the aluminium thermal spray coatings hold more promise in terms of a higher adhesion strength, increased productivity and service life, which can exceed that of the zinc coatings 3-4 times, this being attributed to the aluminium-oxide inclusions contained in the coating.

Comparing reliability of steel structures coated with bitumen and bitumen-rubber materials with that of various metallized coatings was based on studies of the experience gained in operation of pipelines and laboratory studies [1]. Comparing the data on failures of pipelines with different coatings (Fig. 1) shows that for structures subjected to a combined temperature-humidity and soil corrosion effect, such as heat and gas-oil pipelines, the most efficient protection is that with the aluminium metallized coatings.

It should be noted that aluminium coatings also showed themselves to advantage when sprayed on the welds. In this case, in addition to corrosion protection, they make the welded joints more resistant to initiation of solidification cracks, including those within the fusion line region, under repeated static loading in a neutral environment. The presence of an aluminium coating also protects the regions with partial separation of the coating.

Traditionally, aluminium coatings are produced by electric-arc metallizing, or flame or plasma spraying. To protect steel structures, it is common to use electric-arc metallizing or flame spraying. In the majority of cases, coatings produced by electric-arc metallizing are considered to be advantageous over flame sprayed coatings. The method used to apply a coating has an effect on its reactivity and, accordingly, corrosion resistance. Coatings produced by plasma spraying are characterized by the highest quality and corrosion resistance [2]. However, the method of conventional plasma spraying of corrosion-resistant coatings has not found practical application for the well-known reasons, among which the main one is a high cost, including capital and running expenses. Besides, the improvement in the quality of coatings it provides is relatively insignificant.

The progress in plasma spraying and emergence of the commercial high-capacity method of supersonic spraying in the atmosphere of easy-to-get cheap gas mixtures have changed the currently existing priorities [4].

Service properties of plasma coatings depend upon characteristics of the plasma jet and the powder used for spraying. Characteristics of the plasma jet are determined by the choice of the plasma gas, the electric power input into the arc discharge and the plasmatron design. A mixture of fuel hydrocarbon gas (methane, propane-butane) with air is used as the plasma-forming environment. Advisability of using this mixture is associated with a number of technological and economical benefits. Plasma of the combustion products has sufficiently high enthalpy, good transporting properties, and features the possibility of regulating the oxidation-reduction potential. These properties provide formation of an extended plasma jet with a well-filled profile of temperatures and velocity heads and protection of the plasmatron electrodes and the spraying material from oxidation. The jet of the combustion products plasma is characterized by an efficient and uniform heating and acceleration of all particles of the powder, irrespective of their flying path and thermal-physical properties. Life of the output electrode, i.e., anode, of the plasmatron is increased by more than an order of magnitude. This leads to an improvement in the quality of the coatings, increase in the spraying powder utilization factor, rise in productivity of the process and reproducibility of properties of the sprayed coatings.

Gas-air mixtures are readily available in any region or country, where for some reasons it is difficult or expensive to produce high-purity inert gases. Cost effectiveness of using gas-air mixtures becomes more evident with an increase in the capacity of the plasmatron and with an approach to the trans-sonic velocities, where the optimal spraying conditions are shifted to the range of the increased plasma gas flow rates.

Experimental Work

The method of spraying the anticorrosive coatings developed by the authors, based on using the combustion products plasma at the trans-sonic velocities (high-energy plasma spraying) is characterized by high specific properties, i.e., 1 kg of a spraying material per 1 kW power, density of particles in the plasma equal to 20 kg/m3, high productivity - 50 m2/h of the coated surface, new technological capabilities, such as the possibility of producing aluminoceramic or amorphous coatings, and a fundamental (multiple) improvement in service properties of the sprayed coatings.

Composite aluminoceramic coatings are produced by spraying the aluminium and ceramic particles melted in the plasma flow on the preliminarily prepared surface. The plasma sprayed material is formed as a result of deposition of many dispersed particles. With the properly selected spraying conditions all the particles of the aluminium powder are heated until they are completely melted and accelerated to a velocity of 300-500 m/s, while the ceramic particles are heated only to achieve their surface melting and accelerated to a velocity of 200-400 m/s (depending upon the material density). Particle size composition of the aluminium and ceramic powders and parameters of their introduction into the plasma jet are selected so that crushing of the molten particles, collision and coagulation of the aluminium particles with the ceramic particles in flight are minimized (Fig. 2) [5]. This improves fusion of dissimilar materials to form chemical bonds, intermetallic compounds, etc. Upon striking against the substrate surface, the particles are deformed and introduced into irregularities present on the substrate surface to form centres of adhesion. In comparison with aluminium, the ceramic particles have a higher thermal energy content and form in a coating the regions of microfusion with intermetallics. Regions with an increased cohesion bond and density are formed around the ceramic particles. This leads to the formation of a dense aluminium coating, strongly adhering to the substrate, with a porosity of about 0.5 % and with a uniformly distributed ceramic and intermetallic particles. Such coating has an increased corrosion and mechanical properties. The presence of hard ceramic particles in the soft aluminium matrix leads to a multiple increase in mechanical strength and wear resistance of the coating.

The specialized plasma spraying machine is intended for spraying the aluminoceramic coatings on pipes. The machine consists of the following units: plasmatron, double-hopper powder feeder, control panel, power source and a set of mounting and spare parts.

The machine has a modular design. It provides:

- oscillatory ignition of the plasmatron, power turning on, control of the electric current and arc voltage, power turning off;
- turning on, control, adjustment and stabilization of the plasma-forming gas flow rate;
- feeding of water to cool the plasmatron, interlocking and alarm;
- turning on, stabilization and adjustment of the fuel gas flow rate, maintaining the fuel gas to oxidizer ratio on a constant level;
- control of the fuel gas leakage, interlocking and alarm;
- turning on, adjustment and stabilization of the spraying powder consumption.

Specifications of the plasma spraying machine :

Duty cycle, %	100
Plasmatron power, kW	60
Main plasma gas	air
Air flow rate, m3/h	5-15
Auxiliary plasma gas	methane
Methane flow rate, m3/h	0.5-2
Spraying efficiency, kg/h	30
Accuracy of measured feeding of the powder, %	5
Spraying material utilization factor, %	85

The "TOPAS-2" machine equipped with the manually operated plasmatron is intended for spraying the aluminoceramic coatings on connecting parts.

Specifications of the plasmatron:

Power, kW	40
Plasma gas mixture flow rate, m3/h	5-10
Spraying efficiency, kg/h	10

The microplasma machine is used to spray aluminoceramic coatings on tubular joint under field conditions. The machine consists of the following units: plasmatron, remote control panel, powder feeder, machine control panel, power source and independent cooling unit.

At a Customer's request the plasma machine can be optionally equipped with a power source operating from the 380 V, 50 Hz three-phase mains or from the 220 V, 50 Hz single-phase mains, and with a unit for independent cooling of the plasmatron.

Specifications of the microplasma machine:

Duty cycle (cycle duration - 5 min), %	35
Power consumption, kV A	8.5
Working gases: air from the compressor, MPa	0.6
methane, MPa	0.3
Spraying efficiency, kg/h	5

Comparing technical-and-economic indices of different methods used to produced the aluminoceramic coatings is given in Table 1.

Aluminoceramic coatings produced using the plasma machine were tested on a rig by simulating service conditions of pipelines. The coatings were comprehensively tested to check the following parameters:
- heat resistance at a temperature of +150 C;
- heat and moisture resistance at a temperature of 75-80 C and humidity of 100 %;
- resistance to the effect of electric potentials of +0.5 V, -0.5 V, +1.0 V and -1.0 V in the 3 % potassium chloride solution;
- resistance to the effect of acid environments at pH = 2.5 (0.01 % hydrochloric acid solution);
- resistance to the effect of alkali environments at pH = 10.5 (1.25 % sodium hydroxide solution);
- resistance to the effect of salt solutions (3 % potassium chloride solution)

The time of each test was 3000 hours with an intermediate examination every 250 hours. Condition of the coatings was evaluated from such indices as: adhesion (by the grid notch method), impact strength (by weight drop from height of 45 cm), continuity, colour, roughness and structure.

Table 1. Comparison of technical-and-economic indices of different methods for production of aluminoceramic anticorrosive coatings

No.	Indices	Flame spraying	Electric arc metallizing	Traditional plasma spraying	High-energy plasma spraying

1. Gas used	Acetylene, propane-butane + oxygen	Air	Nitrogen, argon + hydrogen	Air + methane
2. Gas flow rate, m3/h	4	90	5	10
3. Power, kW	20	10	30	50
4. Productivity, kg/h	8	12	7	30
5. Spraying material utilization factor, %	80	60	75	85
6. Specific power consumption, kW h/kg	3.1	1.4	5.7	2.0
7. Spraying material	Aluminium powder	Aluminium wire	Aluminium powder	Powder aluminium + ceramics
8. Particle velocity, m/s	50	80	150	300-500
9. Porosity of a coating, %	12	15	8	0.5
10. Strength of adhesion between coating and steel substrate, MPa	15	18	25	35
11. Impact strength, kgf.cm	10	15	20	50
12. Corrosion potential, mV	900	900	750	460
13. Corrosion current density, A/cm2	2 10~~	1 10~~	6.5 10~~	4 10~~
14. Gas-abrasive wear. Weight losses, mg	100	80	40	12

Results

After the heat resistance tests the coatings hardly changed with respect to their initial condition, they preserved their initial colour and structure. No cracks or delaminations were revealed. The level of adhesion did not change, impact strength was somewhat decreased from its initial value of 50 kgf.cm and at the final stage was equal to 45 kgf.cm.

Changes in colour of the coatings were registered after 500 hours of the heat and humidity resistance tests. The coatings became darker with the formation of small regions of black and yellow-brown colour. Testing for another 750 hours and up to the end showed no changes in the condition of the coatings. No fracture, swelling or delamination occurred. Ductility, adhesion and impact strength remained on the initial level. No traces of corrosion were found on the surface of metal samples after removal of the coatings.

Subjecting the coatings to the effect of anode (+0.5 and +1.0 V) and cathode (-0.5 and -1.0 V) potentials showed that after 500 hours the coatings changed in colour (from silver to dark gray). White deposits were formed in the grain spacings. Upon completion of the tests, a local decrease in thickness of the coatings equal to 35-45 microns was registered, but no traces of corrosion on metal under the coatings were found.

Changes in the condition of the coatings subjected to the effect of the acid environment were fixed after 1500 hours. After the end of the tests the coatings preserved their granular structure, the metallic lustre persisted at the grain apexes. Accumulation of white oxides was noted in the grain spacings. The coatings did not fracture, no swelling or delamination was detected. Adhesion and impact strength remained on the initial level.

After testing for 1000 hours in the alkali environment the coatings exhibited a white residue in the form of salt deposits which grew with time. Final examination after 3000 hours showed that the entire surface of the coatings was covered with a crystalline white residue, under which a layer with the metallic lustre was located. No fractures in the form of swelling or delamination were detected, no corrosion processes took place. Adhesion and impact strength of the aluminoceramic coatings remained on the initial level.

Changes in the coatings tested to the effect of salt solutions were noted after 250 hours. The changes were white crystalline deposits formed in the grain spacings. After 3000 hours the deposits filled all the grain spacings and lapped over the coating roughness. The formed layer had a crystalline structure. After removing this layer, the coating surface was seen to be well preserved, but its metallic lustre became a bit dull. No corrosion processes were observed. Adhesion and impact strength were on the initial level. No delamination, swelling or any other type of fracture were detected.

Discussions

Therefore, aluminoceramic coatings subjected to the effect of the basic service aging factors perform the protective function, hardly change their initial properties. The changes that did take place do not lead to any decrease in protective properties. No substantial dependence of protective properties of the coatings upon their thickness (within the range of 170-400 microns) was found.

Aluminium coatings deposited by the flame spraying method and electric arc metallizing lose their protective properties under the effect of potentials and alkali environments after 1500 hours of testing because of swelling and delamination, which is followed by corrosion of the substrate.

This suggests that the use of aluminoceramic coatings will provide a more than 3-fold increase in corrosion resistance, as compared with aluminium coatings produced by flame spraying and electric arc metallizing. Considering that wear resistance of the aluminoceramic coatings is increased 8-10 times in comparison with traditional thermal spray aluminium coatings, one should expect also a fundamental increase in reliability and service life of pipelines with the aluminoceramic coatings.

Aluminoceramic coatings are indicated for the use as anticorrosive coatings on underground and underwater pipelines.

The commercial technology is available now for deposition of aluminoceramic coatings on pipes 100-1200 mm in diameter [6]. These coatings widen the traditional application fields.

Investigations conducted suggest that aluminoceramic coatings hold promise for severe operation conditions, for instance, for protection of channel-free underground and underwater main pipelines subjected to the effect of soil corrosion, erosion and stray currents.

Other anticorrosive coatings

Coatings produced using the supersonic plasma spraying equipment are characterized by a low porosity of 0-1 %, high adhesion strength of up to 150 MPa and a specific microstructure. This enables the problems of high-temperature corrosion, corrosion-erosion and corrosion-cavitation wear, increase in wear and corrosion resistance under conditions of boundary friction, etc. to be solved on a new level, using materials that ensure a passive protection, rather than the direct active protection. In this case, the basic factor which affects protective properties of a coating is the open porosity. Figure 3 [7] shows the dependence of the complete passivation current density upon the porosity of a chromium coating. Coatings with different porosity were produced by different thermal spraying methods: 6-8 % - flame spraying, 3-4 % - plasma spraying in argon-hydrogen atmosphere, 0.5-1.5 % - plasma supersonic and detonation spraying. Chromium coating is the best to protect from hydrogen sulphide, it is characterized by high heat and wear resistance.

Coatings of the Me-Cr-Al-Y system, where Me is Ni, Co or NiCo, have found the wide application for protection of material of the gas turbine engine blades from high-temperature gas corrosion and oxidation. The technology of supersonic spraying such materials makes it possible to produce coatings which are not inferior in heat resistance to detonation coatings.

Table 2. Corrosion characteristics of the Fe55Mo15Cr8Ni2B20 alloy coatings with amorphized structure

Method for deposition of coatings	Amorphous phase, vol. %	Corrosion potential, V	Corrosion current density, j 10~ A/cm2
Plasma spraying (working gas - argon + nitrogen)	75	-0.24	2.0
Plasma spraying (working gas - air + propane-butane)	60	-0.24	2.1
Supersonic plasma spraying (working gas air + methane)	80	-0.20	1.2
Titanium alloy VT1 without coating	0	-0.12	

Investigations of wear of coatings of various materials under cavitation conditions showed that the formation of a dense and strong coating by supersonic plasma spraying was identical to that provided by subsequent annealing in vacuum or laser treatment. During the last years one of the priority areas in the field of coating compositions has been the formation of coatings with an amorphized and fine-crystalline structure. Such coatings have improved service characteristics: adhesion strength, corrosion and wear resistance. Supersonic plasma spraying provides optimal conditions for amorphization of a material. Because of a high velocity of particles (up to 500 m/s) the latter are flattened to ensure the dense contact with the substrate. Corrosion and wear resistance in this case correlate with the amorphous phase content of the coating. Comparing properties of the amorphized coatings sprayed by different methods (Table 2) showed the advantages of supersonic plasma spraying.

Conclusions

1. New anticorrosive aluminoceramic coatings with improved mechanical properties and the commercial technology for high-energy plasma deposition of such coatings were developed.
2. Aluminoceramic coatings subjected to rig testing simulating conditions of operation of pipelines under the effect of basic service aging factors (temperature, combined effect of temperature and humidity, aggressive media and electric potentials) did not change their initial properties and performed the protective function for the entire period of the tests conducted in compliance with "Procedural regulations for rig tests of anticorrosive coatings for underground pipelines".
3. The method of supersonic plasma spraying enables the integrated problems of protection from high-temperature corrosion, corrosion-erosion and cavitation wear, etc., to be solved on a new level, owing to decreasing porosity of the coatings to 0-1 % and using materials which provide a passive protection, rather than the direct active protection.

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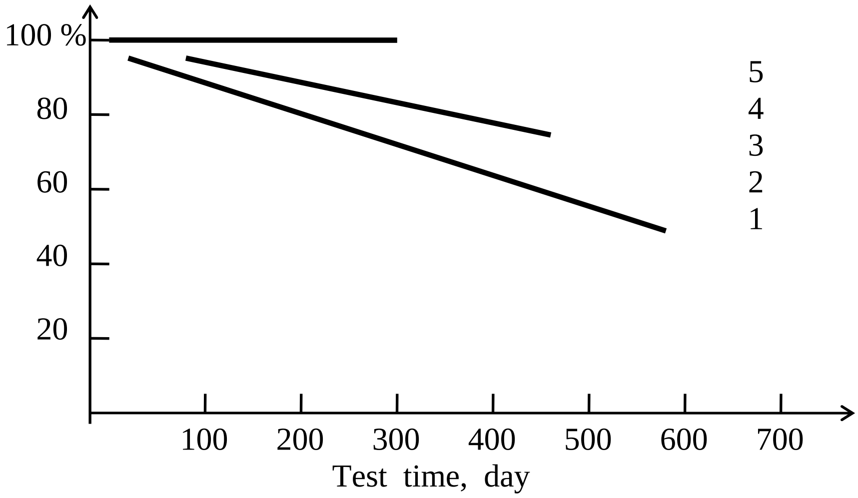

Fig. 1. Comparing failures of pipelines with different types of coatings: 1 - bitumen coatings; 2 - bitumen-rubber coatings; 3 - polyvinylchloride coatings; 4 - zinc coatings produced by thermal diffusion; 5 - aluminium metallizing.

Fig. 2. Coagulation of molten aluminium particles (spherical) with ceramic particles (of irregular shape) in flight. Particles were trapped in water.

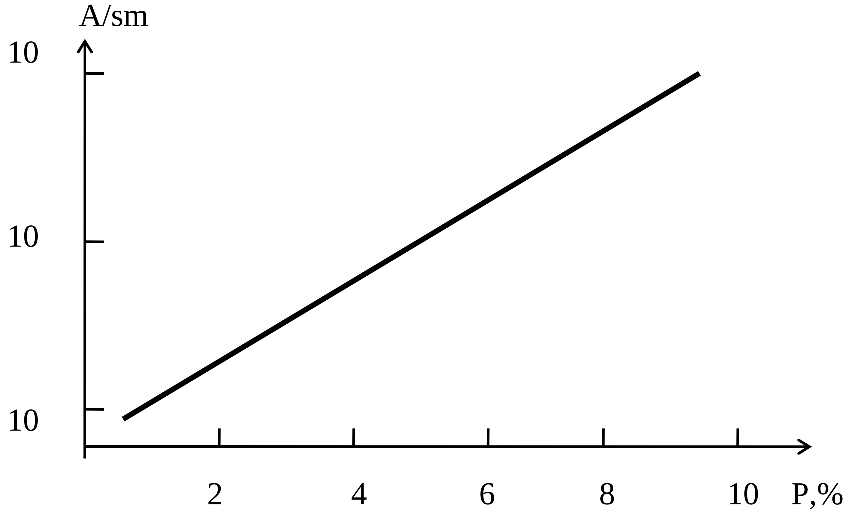

Fig. 3. Dependence of complete passivation current density upon porosity of chromium coating.