ALUMINOCERAMIC CORROSION PROTECTION OF FERROUS METALS

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Protection of ferrous metal parts, structures and constructions from the impact of an environment, involving atmospheric, underground and underwater corrosion, is a pressing and very difficult problem. In addition to direct losses sustained by economies of countries due to corrosion, they also suffer from environmental and mechanical accidents. The situation should not be underestimated. Achievement of a progress in this area requires an integrated approach to solution of the problem: development of efficient environment-friendly anticorrosive materials and a commercial cost-effective technology for their deposition, building of advanced mechanized and automated equipment for manufacture of coated products, improvement of the technology for fabrication of structures and construction of buildings of elements with protective coatings.

These tasks can be implemented using a new composite aluminoceramic coating, technology for its deposition and the associated equipment. The qualitative leap in improvement of performance of aluminium-based thermal spray coatings was provided by two innovations. The first of them is that a mechanical mixture of aluminium powders and ceramics (Fig. 1) is used as a raw material [1], and the second is that a supersonic flow of plasma of the hydrocarbon gas and hydrogen combustion products is used as a heating and acceleration medium [2]. Transportation of molten particles of aluminium and ceramics in the supersonic plasma flow creates such conditions that in flight to the substrate the processes of their collision and coagulation are intensified to a maximum possible degree. This promotes chemical interaction between dissimilar materials to form intermetallic compounds during an extremely short time (hundredths and thousandths of a second). Upon hitting against the surface treated, the molten particles deform, penetrate into irregularities of the substrate and form adhesion centers (Fig. 2). Compared with aluminium, ceramic particles have a higher thermal energy content and form regions of microfusion with intermetallics along boundaries of the mating surfaces during formation of a coating. Regions with an increased cohesion strength and density are formed around the ceramic particles. These circumstances lead to formation of a dense composite aluminoceramic coating (with a porosity of about 0.5 %), characterized by a good strength of adhesion to the substrate, as well as by a uniform distribution of ceramic and intermetallic interlayers in the aluminium matrix.

Such a coating has improved corrosion-resistant and mechanical properties. The presence of hard ceramic particles in the soft aluminium matrix leads to an increase of many times in mechanical strength and wear resistance.

Implementation of this technology became possible with emergence of the process of supersonic plasma spraying [2,3]. With this process the velocity of spray particles increases from 150-250 to 500-700 m/s, which leads to improvement of all service properties of the coatings. Below we give results of comparative tests of aluminoceramic coatings produced by two methods: subsonic and supersonic air-gas plasma spraying. In both cases the coatings were produced under optimal conditions, ensuring the maximum possible coefficient of utilization of the spray material, i.e. 90 %, and the identical productivity, i.e. 15 kg/h. The coatings were applied to steel plates subjected to preliminary abrasive-jet blasting using electrocorundum. X-ray-phase analysis was performed using the DRON-3M unit in the Co $K_{\alpha,\beta}$ radiation, as well as Cu K_α radiation with a nickel filter. Metallography of the coatings was performed using the "Neofot-32" microscope, while the "Leco" microhardness meter was used to conduct durometric analysis. Electron microscopy was conducted using the scanning electron microscope SEM-515. Element analysis of the samples was done using the X-ray microanalyzer of the "Link" system. Mapping of distribution of individual elements in a structure was performed in a characteristic radiation. Coatings sprayed by different methods were investigated using the JEM 200 CX electron microscope (acceleration voltage 200 kV). Foils for transmission electron microscopy were prepared by ion thinning with ionized argon flows.

Thickness of the subsonic and supersonic plasma coatings is 250-300 μm. Microstructure of the coatings is shown in Fig. 3. Separation of a coating from the substrate in the first sample amounts to about 50 %. The second sample is characterized by a tight adhesion to the substrate, its joining line has a relief character, which is caused by preliminary abrasive blasting of the substrate surface, and adhesion strength is equal to 40 MPa.

In both samples no cracks were optically detected in the coating material.

Pores in the coatings were not detected optically with the section preparation methods employed. This is attributable to the fact that aluminium is a ductile material, and it is likely that pores are healed in the process of making the microsections.

Structure of the coatings in both cases consists of an aluminium matrix and dark-gray inclusions of differing sizes and morphologies (Tables 1, 2).

Coarse inclusions in coatings produced by the first method are much larger in size (about 150 μm) than those of coatings produced by the second method, where their size is approximately 65 μm on the average.

Microhardness of this type of the particles (individual coarse ones) in the first sample is 1.3 to 1.8 times as high and amounts to 4210-4550 MPa, whereas in the second sample it is 2370-3510 MPa.

Particles of the fragmentation type are from 15x20 to 50x80 μm in size for the first type of coatings and 15x20 to 15x30 μm for the second type of coatings. Volume fraction of particles of the fragmentation shape in the second sample is 1.4 times as low, and they have a much higher microhardness of about 2900-5150 MPa, which is 1.5-2 times higher than that of the same particles (fragmentation type) in the first sample.

Particles of the type of lamellas (molten particles) have an elongated shape and thickness of about 1 to 10 μm on the average. However, their sizes are more discrete than sizes of particles of coatings of the second type. In addition, volume fraction of such molten particles in the second sample is about .20 %, and in the first sample it is about 10 %.

According to the established concepts, the presence of such particles should have a positive effect on mechanical properties of coatings of the second type.

Therefore, comparison of sizes and distribution of different types of particles in coatings shows that volume fraction of inclusions (fragmentation and lamella type) in coatings of the second type is approximately 1.5-2 times as high, and they are distributed more uniformly that in coatings of the second type.

No spalling was detected in the second sample, whereas a partial spalling of a gray component of mostly fragmentation shape took place in the first sample.

Results of scanning electron microscopy allowed determination of composition of the matrix in both types of coatings and, in particular, in different types of particles. Thus, chemical composition of the matrix is approximately identical in both samples (Tables 1, 2). In addition, matrix of the second sample also contains finely dispersed particles with d ~ 1-3 μm (Table 2).

Mean microhardness of the aluminium matrix of the second sample is a bit higher than that of the second sample, and amounts to about 358 MPa, as compared with 320 MPa of the first sample.

Individual coarse particles in both cases contain mostly Fe (40-41 and 54-56) and Ti (54-57 and 43-44) wt. % for the first and second coatings, respectively, and small amounts of

Al, Mn, Cr and Si (Tables 1, 2). Composition of particles of other types is given in Tables 1 and 2.

Comparison of chemical composition of inclusions in their refinement, as well as morphology (from coarse inclusions with a diameter of about 100-200 μm to lamellas with thickness of about 1 to 10 μm), shows the following.

Content of such elements as iron and titanium in inclusions decreases approximately identically in refinement of the inclusions. For the first sample it decreases 1.3 times and for the second sample – approximately 2 times. Besides, the aluminium content of the particles in their refinement increases approximately 15 times in the first sample and approximately 10-20 times in the second sample.

Therefore, optical metallography and scanning electron microscopy show that in the coating of the second sample the hardening phases undergo a more substantial refinement with an increase of approximately 2 times in their volume fraction. Also, variations in chemical composition of these particles take place. Decrease in the iron and titanium content of particles of the second sample occurs more intensively (1.5 times), as compared with the first sample, whereas the aluminium content increases more intensively in particles of the first sample (1.5 times).

Direct transmission electron microscopy of a fine structure provided the following additional information (in addition to that obtained by optical and scanning electron microscopy) on a structure and phase state of the coatings.

Fine structure of coatings of the first type is non-uniform and in some regions contains sub-grains of a rather large size (1.4-1.6 μm) with a low dislocation density in the internal sub-grain volumes ($\rho \sim 2 \cdot 10^9$ cm^{-2}); other zones of the base metal feature different stages of formation of much more dispersed sub-structural components, i.e. cells, blocks and fragments of about 0.15-0.5 μm in size. In addition, the zones of formation of dispersed structures also feature non-uniformity of distribution of dislocations, i.e. from $4 \cdot 10^9$ cm^{-2} to about $6\text{-}8 \cdot 10^{10}$ cm^{-2}. Besides, the character of the dislocation structures is indicative of their non-equilibrium state, which is proved by the absence of stable dislocation configurations in the bulk of grains, sub-grains and along the different types of boundaries (grain and sub-grain). The MeO particles are sufficiently dense and compact.

We should note the presence of microporosity, which also has a non-uniform distribution. Thus, finely dispersed pores with an approximate size of 0.04-0.08 μm are compactly distributed along the grain boundaries (width of such an extended compact is about 0.3-0.5 μm). Chaotically distributed micropores are also characterized by non-uniform sizes, i.e. about 0.17-0.3 μm, and an elongated shape, i.e. pores have an irregular geometrical shape.

Analysis of the character of dislocation lines of the base metal to check the presence of segregation clusters of phase formations failed to detect such clusters (dislocation lines have no segregation contrasts).

Almost no dispersed phases were detected either (none of them were revealed in microdiffraction reflections).

Therefore, direct investigations of a real structure of the first type of a coating show that the coating base metal, its sub-structure, density and distribution of dislocations are non-uniform. Distribution of microporosity is non-uniform either. No formation of new phases (e.g. intermetallic) was detected.

In the second type of a coating oxide particles have signs of mechanical crushing, which is proved (transmission microscopy) by their irregular shape, acute and non-smoothed angles and cleavages of individual fragments of the particles. Such fragments of the MeO particles are about 0.5-2.0 μm in size.

Diffraction microanalysis of the sufficiently thinned regions of oxides indicated to occurrence of the reduction processes in the above phases. This fact is proved also by structural analysis, i.e. the discrete metal islands are clearly seen against a background of the MeO particles. The presence of metal reflexes against a background of oxide reflections is also seen in the microdiffraction patterns.

Structure of the base metal is characterized by a well-defined developed fragmentation, refinement of sizes of sub-structural elements (as compared with the first method) and more completed sub-structural transformations. This is proved by formation of more perfect sub-structural boundaries and a much more expressed disorientation of sub-structural elements. Such elements as cells are also present, though in a lesser amount. They are characteristic of early stages for formation of structures. Sub-grains and fragments with a size of about 0.15-0.5 μm make up a larger volume.

Dislocations in a coating of the second sample have a much higher density (~ $4\text{-}6 \cdot 10^{10}$ cm^{-2}), distribution of dislocation density being comparatively uniform.

It should be especially noted that very finely dispersed phase formations hundredths of a micron in size and segregation clusters are present along the dislocation lines. Judging from a characteristic arrangement of reflexes in microdiffraction reflections, such phase formations can be identified as intermetallics. It should be noted at this point that a very low intensity of reflexes is indicative of the fact that the process of formation of intermetallics is at the initial stage, as well as at the stages of formation of preliminary precipitates (where the segregation clusters initiate processes of formation of new phases).

It is likely that the uniformly increased dislocation density in a coating is related to a considerable degree to the processes of phase formation, as the segregations and dispersed phases serve as significant barriers which hamper the processes of redistribution of crystalline lattice defects and, accordingly, decrease in the dislocation density. In fact, for the second segregation method the ultra-dispersed phases formed in the coating formation process are the factors that stabilize structure and sub-structure.

Another factor characteristic of the coating structure is the presence of finely dispersed micropores with a size of about 0.05-0.2 μm, which are uniformly distributed in the bulk. The majority of the pores have a globular shape, which indicates that porosity is of an equilibrium and mostly residual character (the final stage of healing of pores).

Investigations performed by the optical metallography, scanning and transmission electron microscopy methods allow some conclusions regarding properties of the coatings investigated.

Judging from structure, morphology peculiarities and distribution of inclusions and phases, it can be suggested that a coating sprayed by the supersonic method will have a higher strength properties (which is provided by a more finely dispersed structure and sub-structure, uniformly increased dislocation density, presence of highly dispersed new phases and finer non-metallic inclusions of the MeO type). General refinement of structural elements (sub-grains) should also favour an increase in ductile properties, while dynamics of the crystalline lattice defects (increase in density of dislocation and subsequent processes of their active redistribution during relaxation) suggest an increase in adhesive properties of the substrate-coating system.

According to the current concepts [4], corrosion protection of ferrous metals using coatings is determined by the following factors: mechanical insulation of metal from an aggressive environment, adhesion of a coating to a workpiece to prevent formation of a new phase (rust) at the metal-coating interface, inhibition of electrode reactions which cause the corrosion process by creating prerequisites for passivation of metal, and structural transformations in the coating which determine its properties.

The above comparative analysis of an aluminoceramic coating shows that all the said factors do act in a coating produced by the supersonic method. Such a coating can be assumed to consist of many uniformly distributed microgalvanic cells (Fig. 4). Here the point is that they contain chemically active non-equilibrium structures which form different-polarity galvanic cells in electrolyte solutions. For example, potential of aluminium in soft water is positive with respect to steel. Steel will destroy in such a galvanic medium. In sea and some types of fresh water, especially that containing Cl^- and SO_4^{2-}, potential of aluminium becomes more negative, which can result in a change in polarity of the aluminium-iron pair. In this case aluminium will destroy.

As the aluminoceramic coating produced by the supersonic plasma method on the whole adheres well to the substrate and tightly fits it, and microgalvanic cells contained in it comprise more chemically active materials, based on kinetic conditions the rate of corrosion (causing transition of metal to chemical compounds) of a material of microinclusions in a composite structure of the coating is much higher than along the substrate-coating interface. The new phase formed fills up discontinuities and voids in the coating due to a wedging effect. Total sealing of the coating occurs, resulting in its passivation and inhibition of electrode reactions. Depending upon the composition and activity of a corrosive environment, these processes complete within several weeks or months. Insoluble residue tightly plugs up the pores and covers surface roughness, preventing access of an aggressive medium to metal. Therefore, the aluminoceramic coating produced by the supersonic method is protective and passivating.

This mechanism is confirmed by the results of tests of the aluminoceramic coatings conducted in bench simulation of service conditions of underground and underwater pipelines. Coatings for the tests were produced using the supersonic plasma spraying machine "TOPAS-180" [2]. The round-robin tests included evaluation of the following parameters:

- heat resistance at a temperature of +150 ^{o}C;
- heat and moisture resistance at a temperature of 75-80 ^{o}C and humidity of 100 %;
- effect of electric potentials of +0.5 V, -0.5 V, +1.0 V, -1.0 V in 3 % solution of potassium chloride;
- effect of acid media at pH = 2.5 (0.01 % solution of hydrochloric acid);
- effect of alkaline media at pH = 10.5 (1.5 % solution of caustic soda);
- effect of salt solutions (3 % solution of potassium chloride).

Duration of each type of the tests was 3000 h, including periodical examinations every 250 h.

The state of the coatings was evaluated by the following indicators: adhesion (by the grid shear method), impact hardness at a weight dropping from a height of 45 cm, density, color, roughness and structure.

After completion of the heat resistance tests the coating hardly changed its initial state, its colors and structure persisted, no cracks or separations were formed, the level of adhesion did not change, impact strength decreased a bit and was 45 kgf·cm at the final stage.

During the heat and moisture resistance tests a change in the coating color was fixed after 500 h. It became darker, and fine formations of a black and yellow color were seen. Further on, after 750 h and up to the end of the tests no changes in the coating state were noted. No fracture, swelling and separation of the coating were fixed. Ductility, adhesion and impact strength remained at the initial level. No corrosion traces were revealed on the sample metal after removal of the coating.

After 500 h of the tests the anode (+0.5 and 1.0 V) and cathode (-0.5 and –1.0 V) potentials resulted in a change in the coating color (from silvery to dark-gray). Deposits of a white color were formed in intergranular spaces. A local decrease of 35-45 μm in thickness of the coating was fixed after the end of the tests, no corrosion traces were seen on the sample metal under the coating.

Beginning of changes in the coating state during the tests to acid medium resistance was fixed after 1500 h. After the end of the tests the coating retained its granular structure, metallic lustre persisted at apices of the grains, a cluster of white oxides was formed in the intergranular spaces, and no damage, swelling and separation of the coating were revealed. Adhesion and impact strength remained at the initial level.

After 1000 h of the tests in alkaline medium a white film was formed on the coating, consisting of salt deposits, which increased with time. The final examination after 3000 h showed that the coating over its entire surface area was covered by a white crystalline deposit, the underlying coating surface having a metallic lustre. No fractures in the form of swelling or separation were seen, and no corrosion processes were observed. Adhesion and impact strength of the aluminoceramic coating remained at the initial level.

Beginning of changes in the coating during the tests to the effect of a salt solution was noted after 250 h. Those were white crystalline formations in the intergranular spaces. After 2000 h the deposits filled up the entire space between the grains and covered all surface irregularities. The formed layer had a crystalline structure with a well preserved coating surface located under it, although the metallic lustre decreased to some extent. No corrosion processes were fixed, adhesion and impact strength of the coating remained at the initial level, and no separation, swelling and damage were revealed.

Therefore, the aluminoceramic coating plays the role of protection under the effect of main service aging factors and hardly changes its initial properties. If such changes do occur, they do not lead to a decrease in protective properties. No significant dependence of protective properties of the coating upon its thickness (within a range of 170-400 μm) was fixed.

This coating was initially developed for protection of hulls of ice-breakers, oil platforms and other items operating in heavily or slightly aggressive environments with pH = 2-12 and salt solutions. Along with ensuring corrosion resistance, it had to possess high mechanical properties, such as wear resistance, ability to retain its properties in bending and cold forming, efficient protection of welds and preservation of its protective and decorative properties during entire service life [5].

At present the aluminoceramic coating is applied in Russia for protection of pipes (mostly heat networks) from corrosion. Under stationary conditions the auminoceramic coatings are sprayed on pipes (Fig. 5) using specialized plasma machines "TOPAS-80" and "TOPAS-180", and under field conditions (on pipe joints) – using machine "TOPAS-40" (Fig. 6).

Tests of the aluminoceramic coatings conducted in bench simulation of service conditions of heat network pipelines at Open Joint-Stock Company "ORGRES" of the MINTOPENERGO of Russia showed the following. A coating being tested does not change its initial properties under the effect of the main service aging factors (temperature and a combination of temperature, moisture, aggressive media and electric potentials) and performs the protection function during entire service life (50 years). Coated pieces (Fig. 7) can be operated and held at any ambient temperature, requiring no extra cathode protection.

Based on the tests performed, the aluminoceramic coating was included into a new "Standard Instruction on Protection of Heat Networks from External Corrosion", which was enforced on 01.01.1996. Since 1996 the Kapotnensky base MOSTEPLOENERGOREMONT has been producing pipes and fittings with such coatings with a productivity of 50 km/year for the Moscow needs. The many-year operation experience proves the availability of a new commercial process for deposition of high-quality anticorrosive coatings with increased mechanical properties on external surfaces of pipes. Advantages of the process include high productivity (50 m^2/h for the surface being coated), easy automation, high coefficient of utilization of a spray material (90 %), efficient utilization of the Ukrainian sources of raw materials and low specific power consumption (1 kW/h per square meter of a coating). The process can be used for application of protective anticorrosive coatings with increased mechanical properties on internal surface of pipes, shaped parts, structures and fittings under field conditions.

Specifications of the coatings:

Thickness, mm	0.25-0.3
Strength of adhesion to steel substrate, MPa	35
Impact strength, kgf/cm	50
Porosity, %	0.5

The coatings require no impregnation in operation of heat networks under any conditions. The possibility exists of laying down of coated piped by the channel-free method.

Based on the experience gained, Specifications (TU) and Technological Regulations were developed for the process of plasma spraying of the aluminoceramic coatings on pipes and fittings with a diameter ranging from 57 to 820 mm, and since 2002 the coatings have been included into the SNIP document (Sanitary Code and Regulations).

All that stimulated a new stage in widening of the scope of application of the aluminoceramic coatings in Russia and construction of a factory of the Open Joint-Stock Company "AKOR" in Ulianovsk, specializing in production of anticorrosion and heat- and water-proof insulation protection of pipes and shaped parts intended for construction of heat and water supply systems, gas and oil-products pipelines, industrial and field pipelines [6].

The "AKOR" Company factory was constructed under the targeted program of the Russian Joint-Stock Society "Unified Power System", funded by almost two tens of regional power supply companies. Opportune and complete financing of the construction enabled the objects to be commissioned and production to be started up within the proper time schedules.

Products of the factory are intended for implementation of the resource saving technologies.

Anticorrosion and heat- and water-proof insulation protection of pipes provides a long-term strength, operational reliability and power saving. The use of protected pipes provides a high cost effectiveness in renewal of municipal water, heat and gas distribution lines.

Pipes with the internal aluminoceramic coatings allow avoidance of abrasive wear and deposition on the pipe walls of paraffin, polymerization products and other residues, ensuring the high quality and cleanness of a product being transported, an increase in capacity, utilization of smaller-diameter pipes, decrease of up to 20 % in consumption of power for transportation, elimination of losses of a product because of repair of pipe systems and decrease in the risk of environmental pollution and accidents.

The factory constructed is a test ground for optimization of new technological processes for corrosion and heat protection of pipelines, aimed at accomplishment of the Ulianovsk district gasification program, among other things.

The use of anticorrosive aluminoceramic and protective polyurethane foam coatings for heat network pipes allows:

- extra decrease of 7-15 % in thermal energy losses in transportation;
- increase of 3 times in reliability of heat supply for the needs of population and industry;
- decrease in the rate of low-temperature catastrophes and accidents in heat networks and a respective increase in reliability of operation of heating turbogenerators at heat power plants;
- decrease in length and quantity of annually renewed networks and reduction of 50-70 % in capital costs for earthwork;
- decrease of 40-60 % in consumption of steel pipes;
- reduction of impact on the environment due to decrease in ejection of combustion products, thermal pollution of the environment, elimination of defrosting and

erosion of soil over substantial surface areas, and mitigation of the impact of high-temperature accidents on the environment.

Specialized investigations of protective properties of the aluminoceramic coatings were carried out in 2001 at the chemical protection laboratory of VNIIGAS, Moscow, resulting in recommendations for their application at the gas industry objects, such as pipes with different types of active-passive protection, including surface pipelines under atmospheric corrosion conditions, service lines at industrial sites in the alternating wetting zones (at the earth – air boundaries) and different types of field pipelines.

The Russian Joint-Stock Company "ROSNEFTEGASSTROJ" recommends that design institutions and industrial organization consider, while selecting a method for corrosion protection of pipelines, including gas, oil and oil-products pipelines, the use of the RPE "TOPAS" technology and equipment for deposition of aluminoceramic coatings on pipes and fittings.

Conclusions:

1. Available are the new anticorrosive aluminoceramic coatings with increased mechanical properties and the commercial technology for supersonic plasma spraying of such coatings.
2. Bench simulation of service conditions of pipelines showed that the aluminoceramic coatings did not change their initial properties under the effect of main service aging factors (temperature and a combination of temperature and humidity, aggressive media and electric potentials) and would perform the protection function during the entire service period (not less than 30 years).
3. Owing to decreasing the coating porosity to 0-1 %, the supersonic plasma spraying method allows the integrated problems of protection of structures from corrosion, corrosion-erosion, cavitaion wear etc. to be solved at a new level by providing both protective and passivating shielding film on the surface.

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