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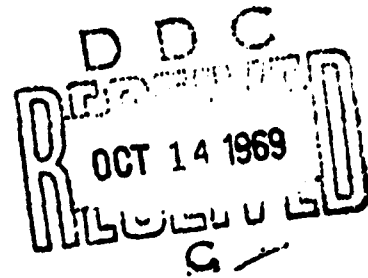
FOREIGN TECHNOLOGY DIVISION



DEPOSITION OF REFRACTORY COATINGS WITH THE USE OF PLASMA

by

T. A. Nimvitskaya and S. L. Fishman



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ABSTRACT

(U) The effects of metal surface preparation and of plasma deposition conditions on the properties of deposited refractory coatings were examined. The coating of low and medium carbon steel with aluminum oxide (30-70 micron) or aluminum oxide containing oxygen-resistant enamel E-1 or base enamel 2015/3132 was carried out using plasma apparatus UMP-3-63 and argon, nitrogen, helium, or their mixtures as plasma-forming gases. Optimum distance between plasma generator and surface of the material to be coated was 150-200 mm. Comparison of different gas mixtures showed the mixture of nitrogen plus 10 percent helium most effective. The metal surfaces were prepared by various methods --sandblasting with subsequent sodium nitrite passivation, sulfuric acid etching at 70 C with washing and neutralizing, chemical nickel or cobalt plating, or conventional coating with base enamel 2015/3132. Plasma deposition of the aluminum oxide onto the nickel- or cobalt-plated metal resulted in poor adherence to the metal. Deposition onto the enamel-primed material gave coatings with good impact resistance that withstood thermal cycling better than did coatings deposited directly on the metal. Orig. art. has: 4 tables and 3 figures.

DEPOSITION OF REFRACTORY COATINGS WITH THE USE OF PLASMA

T. A. Nimvitskaya and S. L. Fishman

The majority of the processes in ferrous and nonferrous metallurgy proceed at very high temperature and the problem of their intensification - and sometimes even their realization - is frequently connected with the need to seek means of protecting the structural materials from the corrosive effect of the ambient medium. In connection with this, the creation of nonporous and low-porosity heat-resistant coatings for steel structures in metallurgical plants is particularly urgent.

Crystalline protective coatings of highly refractory oxides, silicates, nitrides, carbides, borides, and other refractory compounds possess very high refractoriness, good erosion resistance, and high thermal protection properties. With existing methods of depositing the coatings (gas-flame and plasma) they are often porous, which reduces the protection of the metal from oxidation. It is known that the porosity in coatings applied by the plasma method is less than that in coatings applied by the gas-flame method.

Our work is concerned with the study of the influence of the conditions of plasma deposition of a coating on its properties and with preparation of the metal surface.

For applying the coatings we used the plasma unit UMP-3-63, with certain alterations.

Argon, nitrogen, helium, and their mixtures were used as the plasma-forming gases while the coating material was pure aluminum oxide (particle dimensions 30-70 μm) and aluminum oxide with additions of the oxygen-resistant coating enamel E-1 or the base enamel 2015/3132, which are usually used in enameling chemical apparatus [1]. The compositions of these enamels are given in Table 1.

The coatings were applied on low-carbon and medium-carbon steel. Preliminary steps included experiments to determine the selection of optimum flow rates of plasma-forming gas, flow rate of the gas for feeding the atomized material, diameter of the plasma-forming channel of the plasma generator, distance from the plasma generator to the specimen, and other parameters of the process, as well as details of the structure of the plasmatron.

The optimum flow rate of the plasma-forming nitrogen was achieved with its pressure in the system equal to 19.6 N/cm^2 (2 kg/cm^2).

The optimum flow rate of nitrogen for feeding the powdered material was obtained with an excess pressure of nitrogen in the feeder of $0.6\text{-}1.0 \text{ N/cm}^2$ ($0.06\text{-}0.10 \text{ kg/cm}^2$). At a higher pressure the powder particles were poorly melted and the coating was porous.

To determine the optimum distance from the plasma generator to the coated surface, a layer of aluminum oxide was placed on flat low-carbon steel specimens 2 mm thick, which were placed at a distance of 100, 150, 200, and 250 mm from the plasma generator. The obtained coatings were examined under an MBS-1 microscope with a magnification of 68 to determine the degree of melting of the spray-coated particles, their adhesion to one another, and the uniformity and solidity of the coating.

Petrographic investigations showed that the obtained coatings consisted of 85-90% $\gamma\text{-Al}_2\text{O}_3$ and 10-15% $\alpha\text{-Al}_2\text{O}_3$.

Owing to thermal stresses there was exfoliation of the coating from the metal in specimens coated at a distance of less than 100 mm from the plasma generator. No gaps were detected in the aluminum oxide

layer; the melting of the particles was satisfactory. The best results were obtained with specimens which were 150 and 200 mm from the plasma generator. No exfoliation of the coating from the metal was observed in this case. In specimens located 250 mm from the plasma generator gaps down to the metal were visible in the coating; the adhesion of the particles to each other was weaker than in the preceding cases. The further the specimen was placed from the plasma generator (with the same duration of spray coating) the thinner was the obtained coating, owing to partial escape of the sprayed particles from the stream of gas.

Table 1. Chemical composition of enamels.

Components of enamel	Enamel composition, wt. %		
	2015	3132	3-1
SiO ₂	42.83	45.00	58.13
TiO ₂	4.92	5.00	7.75
B ₂ O ₃	18.24	26.80	1.94
Al ₂ O ₃	6.40	2.00	2.14
CaO	5.00	1.00	4.36
Na ₂ O	11.92	12.30	15.25
K ₂ O	4.41	1.20	2.42
Na ₂ SiF ₆	3.94	—	—
CaF ₂	—	3.70	—
CO ₂ O ₃	0.56	1.80	0.87
MnO ₂	1.24	0.60	—
Ni ₂ O ₃	0.54	0.60	—
Na ₂ AlF ₆	—	—	7.14

Note: For preparation of the slip the base enamel 2015/3132 was ground with the following additives (g): enamel 2015, 70; enamel 3132, 30; Chasov Yar clay, 6; ammonium molybdate, 0.4; potassium carbonate, 0.2; water, 40.

In comparing coatings of aluminum oxide obtained with argon and mixtures of nitrogen and helium, argon and helium, and nitrogen and argon used as the plasma-forming gas, it is necessary to note that the best results are obtained in those cases when the nitrogen/helium mixture containing approximately 10% helium is used.

In studying the effect of the method of surface preparation and the influence of the nature of the metal on adhesion of the coating to it we used various forms of preparation of the metal surface:

1) Hydraulic sandblasting with subsequent passivation in a solution of sodium nitrite;

2) etching in a solution of sulfuric acid with a concentration of 80 kg/m³ at a temperature of 340°K (70°C) up to complete removal of scale with subsequent washing in water, removal of slurry by rubbing, and neutralization in an alkali solution;

3) chemical nickel plating in an acid solution;

4) chemical cobalt plating;

5) application of a layer of base enamel 2015/3132 by the usual enameling methods.

The mechanical strength of the coating and its adhesion with the steel or the layer of nickel and cobalt was determined by the impact method: we calculated the work of impact of a sphere weighing 87.5 grams, dropped on the surface of the specimen from a height of 0.75 m, up to the moment of destruction of the coating. The results are given in Table 2. The strength of adhesion of an aluminum oxide coating with the metal was adequate when sandblasting treatment of the surface was applied.

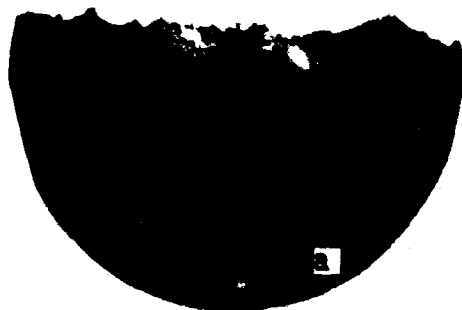
Table 2. Results of impact testing of specimens for adhesion strength.

Material of specimen	Plasma-forming gas, pressure, M/cm ²	Distance from plasma generator to specimen, mm	Impact work, J	Remarks
Sandblasted steel	He 3.9+ N ₂ 19.6	150	Over 33.7	
		100	Over 30.2	Chipping of part of enamel layer
Steel coated with enamel 2015/3132	He 19.6+ N ₂ 19.6 N ₂ 19.6 Ar 19.6+ N ₂ 19.6	200	1.4	
		125	Over 30.2	
		110	Over 30.2	Chipping of part of enamel layer
		120	Over 30.2	
		200	2.0	

Remark. Nitrogen was fed through a nozzle 1.5 mm in diameter; argon and helium were fed through a nozzle 0.5 mm in diameter.

With preliminary chemical application of nickel layers, poor attachment of the coating to the metal was observed at the moment in which the coating was sprayed on. A somewhat better coating was formed on a surface covered with a layer of cobalt.

Preliminary application of a layer of base enamel made it possible to create a coating which was impervious to gas and improved the strength of the coating-metal adhesion; it should be noted that the best adhesion was obtained with a distance of the metal from the plasma generator equal to 100-150 mm. Impact work equal to 30 J did not lead to delamination of the aluminum oxide from the enamel. When the distance was increased the adhesion was weaker. Delamination occurred with a work of impact equal to 1.2 J. The strength of the enamel layer without the aluminum oxide comprised 0.38 J (at first sign of destruction of enamel).



NOT REPRODUCIBLE

Fig. 1. Metal/coating boundaries and boundary between coating layers. a - metal/aluminum oxide, mag. 315; b - metal/base enamel 2015/3132/aluminum oxide with addition of 20% E-1 enamel, mag. 200.

NOT REPRODUCIBLE



Fig. 2. View of two-layer coating of base enamel 2015/3132 and aluminum oxide after heat treatment. a - 1073°K (800°C), 0.5 h, mag. 400; b - 1073°K (800°C), 6 h, mag. 200; c - 1223°K (950°C), 6 h, mag. 315.

Tests on thermal stability were carried out with heating up to temperatures of 873-1073°K (600-800°C) followed by sharp cooling down to 293°K (20°C). In this case a layer of aluminum oxide applied directly on the metal was subject to exfoliation, while under identical conditions (an equal number of temperature changes) a layer applied with preliminary application of a layer of base enamel was held firmly on the metal.

A metallographic study was made of the metal - coating boundary. Fig. 1a shows the aluminum oxide/metal boundary where the coating was applied by means of plasma. No products of interaction of aluminum oxide with the metal were detected; clearly, in this case the adhesion of the coating to the metal has a purely mechanical character.

Figure 1b illustrates the same boundary for the case when aluminum oxide with addition of 20% E-1 enamel was applied with the help of a plasma on to an intermediate layer of base silicate enamel 2015/3132. In this case the boundary between the enamel and the aluminum oxide is completely even; there is no developed relief.

With subsequent heating interaction of the aluminum oxide with the enamel begins. A two-layer coating was subjected to heat treatment at a temperature of 873°K (600°C) for 0.5 and 2 h. No changes were noted on the boundary with holding for 0.5 h. Holding for 2 h lead to the appearance of a finely dispersed phase in the base enamel; it consisted of particles with a prismatic and rhombic shape. This phase was located to a large degree at the enamel/plasma coating boundary. Petrographic investigations* established that this crystalline phase is a product of the interaction of silicon dioxide found in the enamel with the aluminum oxide and is an anisotropic silicate phase of the type of andalusite $\text{SiO}_2 \times \text{Al}_2\text{O}_3$.

*Petrographic investigations were carried out by L. P. Kulikova, Engineer.

Heat treatment at the higher temperature of 1073°K (800°C) led to the appearance of the finely dispersed phase even with holding for 0.5 h (Fig. 2a). With holding for 6 h we observed principally aluminum silicate phases of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mulite), spinelide phases of the complex composition $\text{MeO} \cdot \text{R}_2\text{O}_3$, and a phase of the andalusite type, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (Fig. 2b).

With heat treatment at a temperature of 1223°K (950°C) the same phases were observed as at the 1073°K (800°C) temperature; however, the predominant phase was the spinel, grouped at the enamel - aluminum oxide boundary (Fig. 2c).

Thus, with heat treatment of the coating at a temperature of 573-1073°K (600-800°C) chemical interaction occurs between the various components of the coating, improving the bond between its layers. Heat treatment at a temperature of 1223°K (950°C) leads to a chemical reaction between layers, with internal stresses appearing within the coating and leading later to exfoliation of the coating.

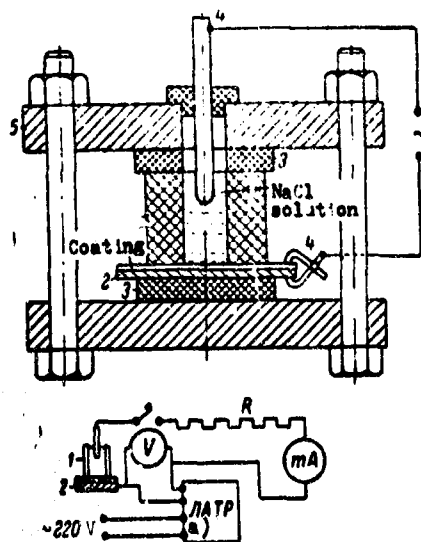


Fig. 3. Diagram of installation for determining the permeability of coatings applied by means of plasma.
KEY: a) Laboratory Autotransformer.

*[sic].

In order to evaluate the permeability of the coating with respect to fluid and gaseous media we prepared the unit depicted on Fig. 3. The specimen formed the bottom of an electrolytic cell filled with a 10% solution of sodium chloride. Voltage was fed to the specimen and to an electrode inserted in the cell from a source of industrial-frequency ac current. A current of one or another force appeared in the cell; the force was dependent on the number and diameter of coating pores which penetrate through to the metal. The magnitude of the current passing through the coating pores characterizes the permeability or porosity of the coating.

Table 3. Effect of coating thickness on its permeability.

Surface preparation	Coating thickness mm	Permeability (el. cur., mA)
Sandblasting	0.27	76.5
	0.30	75.0
Etching	0.30	77.5
	0.40	74.5
	0.44	75.5
Cobalt plating (180 s)	0.18	83.5
	0.27	82.5
	0.37	77.0
Cobalt plating (300 s)	0.22	83.0
	0.24	80.0
	0.27	79.5
Cobalt plating (600 s)	0.20	85.0
	0.23	82.5
	0.27	78.0
Nickel plating (180 s)	0.30	84.5
	0.39	78.0

Remarks. Coating application conditions: plasma-forming gas, nitrogen; distance from plasma generator to specimen, 150 mm; power, 14.3-21 kW. With chemical deposition we obtained a nickel layer 16 μ m thick in 3600 s; the cobalt layer was 5 μ m for the same time.

Table 3 shows the results of measurements of permeability of aluminum oxide plasma coatings. To judge by the experimental results, with an increase in the aluminum oxide layer thickness from 0.18 to 0.47 mm the permeability of the coating is somewhat decreased. However, it is not possible to obtain a completely impermeable coating of aluminum oxide.

No permeability was detected by this method in coatings applied on a base layer of enamel 2015/3132.

The total porosity of the aluminum oxide layer was determined by hydrostatic weighing, i.e., by filling the pores with water according to a known procedure [2]. The results of determination of total porosity are given in Table 4.

The smallest porosity, equal to 4.35%, was obtained when a mixture of nitrogen with helium was used as the plasma-forming gas.

Table 4. Porosity of aluminum oxide layer applied by the plasma method on a layer of base enamel 2015/3132.

Plasma-forming gas	Gas pressure in feeder, N/cm ²	Distance from plasma generator to specimen, mm	Porosity, %
Argon 19.6 N/cm ² + + nitrogen 17.6 N/cm ²	0.8	100	7.75
		120	20.0
		150	21.6
		200	44.3
	1.0	100	16.4
		200	19.9
Argon 9.8 N/cm ² + + nitrogen 19.6 N/cm ²	1.0	100	20.8
		150	29.8
		200	23.4
Nitrogen 19.6 N/cm ²	0.8	150	27.6
Nitrogen 19.6 N/cm ² + + helium 9.8 N/cm ²	0.8	100	4.35
		200	9.8
Nitrogen 19.6 N/cm ² + + helium 19.6 N/cm ²	0.8	100	12.1
		150	9.7
		200	25.8

A quantity of 20-50% E-1 enamel was added to the aluminum oxide in an effort to improve the density and the strength of coating-to-metal adhesion. However, experiments showed that the adhesion strength of such a coating was not essentially increased. The porosity of the coating was somewhat reduced after heat treatment at temperatures of 873°K (600°C) and above, owing to flowing of the enamel and its reaction with the aluminum oxide.

The increase in coating density achieved by preliminary application of a layer of base enamel 2015/3132 leads to improved corrosion

resistance of the coating. A layer of aluminum oxide applied directly on the metal with heating in an atmosphere of air does not have a protective effect: a layer of iron oxide forms under the layer of aluminum oxide. The same coating applied on a layer of enamel can have a protective effect. For a further increase in the heat resistance of a two-layer enamel - aluminum oxide coating it is necessary to select a silicate enamel with an increased temperature of initial softening, since the temperature at which such coatings can be used is determined by the properties of the enamel - its softening point and its reactivity with respect to aluminum oxide and the protected metal.

In summing up the results of the experiments on applying coatings with the help of a low-temperature plasma, it can be concluded that this method is unconditionally promising as a procedure for applying two-layer coatings to protect metals, in particular steel, from the action of the atmosphere at high temperatures and also from the effect of molten media which do not dissolve aluminum oxide.

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