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The effect of plasma coatings on the properties of low-alloy steels

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The paper considers the possibility of using ion-plasma spraying of coatings on low-alloy steels 4X5MFS and 5XNM. The choice of these grades is due to the fact that they do not contain tungsten, given the sharp increase in its deficiency, and the molybdenum content is limited, and these steels also meet the requirements for the substrate material on which the titanium nitride coating is applied. The coatings were applied by the method of condensation of the substance under ion bombardment conditions. To determine the required nitrogen pressure, titanium nitride is applied at different partial nitrogen pressures – from $3{\cdot}10^{-3}$ to 1 Pa. Coatings obtained under different nitrogen pressures differ in the amount and size of the droplet phase. The largest amount of the droplet phase containing α-Ti is observed in coatings obtained at nitrogen pressures of $3{\cdot}10^{-3}$ Pa, $3{\cdot}10^{-2}$ Pa. An increase in nitrogen pressure (4·10–1 Pa, 1 Pa) significantly reduces the level of microdistortions of crystal lattices in the coating, its plasticity increases. In this regard, the fragility of the coating decreases with its sufficiently high hardness. As laboratory tests have shown, a titanium nitride coating applied under optimal technological parameters increases the corrosion resistance of the materials on which it is applied three times, and scale resistance – two to four times.

Keywords: ion-plasma coatings, surface, phase, strengthening, parameters .

Вплив плазмових покриттів на властивості економнолегованих сталей. *Є. Єрмилова, Д.Б. Глушкова, В.М. Волчук*

У роботі розглянуто можливість застосування іонно-плазмового напилення покриттів на економнолеговані сталі 4Х5МФС і 5ХНМ. Вибір зазначених марок зумовлений тим, що вони не містять вольфраму, зважаючи на різке зростання його дефіциту, і вміст молібдену обмежений, а також ці сталі задовольняють вимоги до матеріалу підкладки, на яку наноситься покриття нітриду титану. Нанесення покриттів здійснювалося методом конденсації речовини в умовах іонного бомбардування. Для визначення необхідного тиску азоту нітрид титану наноситься за різних парціальних тисків азоту – від $3{\cdot}10^{-3}$ до 1 Па. Покриття, отримані за умови різних тисків азоту, розрізняються кількістю та розміром крапельної фази. Найбільша кількість крапельної фази, що містить α-Ti, спостерігається у покриттів, отриманих за тисків азоту $3{\cdot}10^{-3}$ Па, $3{\cdot}10^{-2}$ Па. Збільшення тиску азоту (4·10–1 Па, 1 Па) значно зменшує рівень мікроспотворень кристалічних ґраток у покритті, зростає його пластичність. У зв'язку з цим знижується крихкість покриття за досить високої його твердості. Як показали лабораторні випробування, нанесене за оптимальних технологічних параметрів покриття нітриду титану підвищує корозійну стійкість матеріалів, на яке воно нанесено, утричі, окалиностійкість – удвічі–учетверо.

1. Introduction

The use of plasma coatings from wear-resistant materials opens up wide possibilities [1-3]. Among these methods, preference should be given to the method of condensation of matter under ion bombardment conditions (IBC), which allows you to regulate the process temperature (~300–800 °C), which makes it universal and leading among strengthening technologies, due to the fact that the IBC method allows you to regulate the composition of the coating, helps to obtain a coating with low thermal conductivity, reduce the temperature gradient, create compressive stress on the surface, and provide the surface layer with high strength, corrosion and scale resistance characteristics [4-6].

Due to its versatility and high efficiency, the method of condensation of matter under ion bombardment conditions is one of the leading modern surface strengthening technologies [7]. To establish the patterns of the influence of plasma coatings on the thermal endurance of the substrate material, scale resistance, and corrosion resistance, the structure and phase composition of the applied coatings were studied [8]. The paper considers the possibility of using ion-plasma spraying of coatings on low-alloy steels 4X5MFS and 5XNM. The choice of these grades is due to the fact that they do not contain tungsten, given the sharp increase in its deficiency, and the molybdenum content is limited, and these steels also meet the requirements for the substrate material on which the titanium nitride coating is applied.

2. Materials and methods

Titanium nitride was chosen as the coating based on the following indicators [9] :

1. It is resistant to destruction under significant temperature and stress fluctuations.

2. It has high strength properties (modulus of elasticity, microhardness) and retains them even at high temperatures.

3. It has low thermal conductivity.

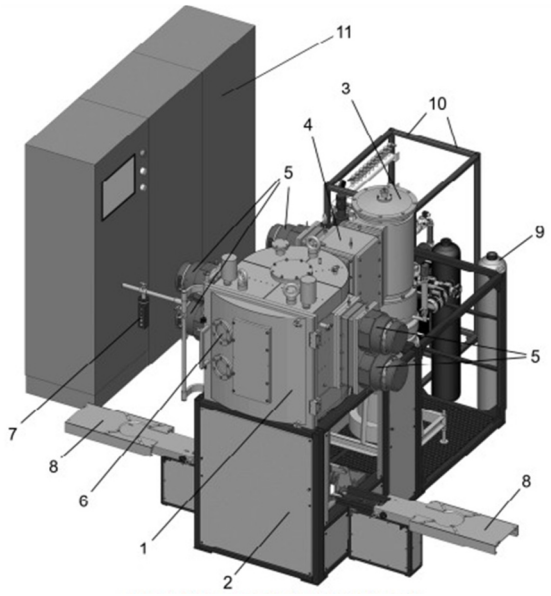

Fig. 1. Key units of the installation Bulat 10: 1 – camera; 2 – stand; 3 – vacuum pumping system; 4 – L-shaped filter; 5 – vacuum-arc plasma generators ; 6 – viewing window; 7 – manual control panel of the loading-unloading system; 8 – horizontal feed table; 9 – cylinders with working gases; 10 – water supply system; 11 – power supply and control cabinet

4. Resistant to high temperature corrosion and oxidation.

5. Consumables (titanium, nitrogen) are not in short supply and are widely used in industry.

Coatings obtained by this method have high stability, low porosity, and good adhesion to the substrate.

The materials selected for the research were 4X5MFS and 5XNM steels, which do not contain tungsten, due to the sharp increase in its deficiency, and the molybdenum content is limited, as well as those that meet the requirements for the substrate material on which the titanium nitride coating is applied (Table 1).

The coating process was carried out on the Bulat-10 installation (Fig. 1). The method of condensation of a substance under ion bombardment conditions includes two key stages:

1. Cleaning, heating, and activating the substrate surface by bombarding it with ions of the

Table 1. Chemical composition of the steels under investigation

Steel	Element content, %				
	WITH	Zr	Mo	V	Ni
5XNM	0.50-0.60	0.60-0.80	0.15-0.30	–	1.40-1.80
4X5MFS	0.37-0.44	4.50-5.50	0.80-1.10	0.80-1.20	–

Table 2. Heat treatment modes of steels 5KhNM, 4Kh5MFS

Steel grades	Hardening					Vacation		
	loading temperature	heating temperature, °C	heating holding time	cooling medium	hardness, HRC e	temperature, 0 C	exposure time, hour, including heating the batch of parts	hardness HRC e
5XNM	700-750	830-860	1-2 min per 1 mm of flow	oil cooling	47-50	500-520	4-5	42-45
4X5MFS		1050-1070			55-61	560-580		42-45

material being deposited, accelerated to the required energy level.

2. Coating deposition with simultaneous ion bombardment of condensate, which contributes to the formation of a coating with optimal performance characteristics [10].

The coating time is one of the important technological parameters that needs to be optimized. The deposition rate of titanium nitride (TiN) coating on the "Bulat-10" installation is 10 μm/h.

Given that the maximum adhesion activity to the substrate and the effect on increasing the thermal endurance of 4X5MFS and 5XNM steels are achieved at a coating thickness within 3–5 μm, the application time varied from 20 to 30 minutes. The hardening process of selected steel grades was carried out at temperature regimes that ensure the dissolution of most of the carbides and the formation of highly alloyed martensite (Table 2).

Such heat treatment allows to preserve the fine-grained structure of the material while maintaining its sufficient toughness. After hardening, the steels were subjected to high-temperature tempering, which contributes to an increase in impact strength and endurance limit. This process also provides additional strengthening due to dispersion hardening [11], accompanied by the formation of finely dispersed carbides and achieving a hardness in the range of 42–45 HRC. When selecting the optimal coating parameters, the pressure of the reaction gas in the installation chamber, the temperature of the substrate preheating, and the duration of deposition were taken into account. As is known, one of the key parameters of the coating deposition process by the condensation method of matter under ion bombardment conditions is the pressure of the reaction gas [12]. The optimal value of this parameter in a vacuum chamber is determined individually for each specific case and depends on the composition of the cathode, the characteristics of the equipment, and the operating conditions of the coated parts [9, 13, 14]. Table 3 shows the parameters of the influence of the ion bombardment temperature on the adhesion of the coating to the substrate.

The strength of the coating to the base metal is one of the main parameters that will determine the characteristics of the coating of the selected composition. The strength of the coating to the substrate was assessed using a method based on the combined plastic deformation of the coating and the substrate when the Rockwell hardness tester indenter is inserted. The strength of the coating to the substrate is judged by the size relative to the area of the coating crack around the imprint. The area is determined on an optical microscope at a magnification of 100 times using an eyepiece with a grid. The strength of the connection Kα was determined by the formula

$$K\alpha = S_0 /(S_0 + S_k), \quad (1)$$

where S_0 – the footprint area of the working surface plane;

S_k – the area of the chipped plane of the working surface.

The range of K values α is from 0 (poor connection) to 1 (with normal quality of connection to the substrate).Thermal endurance, corrosion resistance, and scale resistance were determined according to DSTU.

3. Results and their discussion

The most important parameter of the condensation process of a substance under ion bombardment conditions is the pressure of the reaction gas [12].

It should be noted that the optimal pressure of the reaction gas in the vacuum chamber

Table 3. Effect of nitrogen partial pressure on coating characteristics

Nitrogen pressure, Pa	$3 \cdot 10^{-3}$	$3 \cdot 10^{-2}$	$4 \cdot 10^{-1}$	1
Microhardness, GPa	22	26.0	23 , 0	18 .0
Coating color	gray	yellowish-gray	yellow	brown-golden

Table 4. Effect of nitrogen partial pressure on the thermal endurance of the coating

Steel grade	Pressure				
	without coating	$3 \cdot 10^{-3}$	$3 \cdot 10^{-2}$	$4 \cdot 10^{-1}$	1
	thermal endurance				
4X5MFS	2000	3000	5000	9500	12000
5XNM	2000	3500	5000	9000	11500

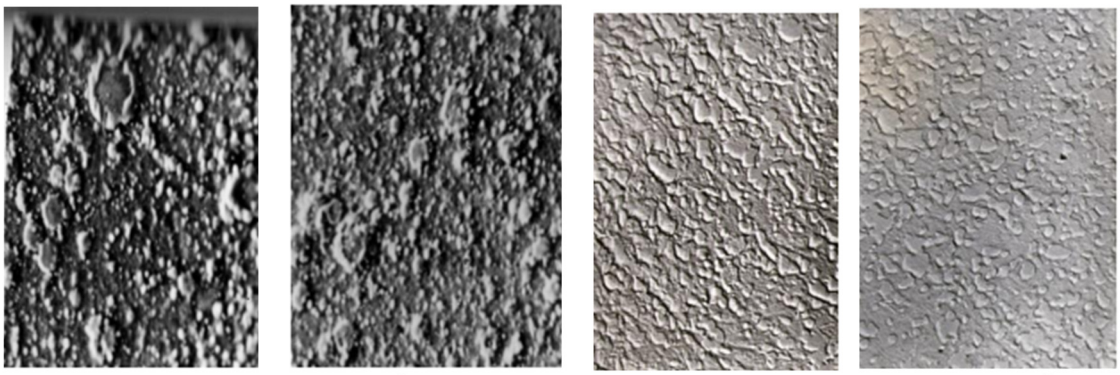

Fig. 2. Surface microstructure of titanium nitride coatings obtained at different reaction gas pressures: a – $3 \cdot 10^{-3}$ Pa; b – $3 \cdot 10^{-2}$ Pa; c – $4 \cdot 10^{-1}$ Pa; d – 1 Pa

must be determined in each specific situation and depends on the composition of the cathode, the model of the installation on which the coating is applied, and the operating conditions of the coated part [9, 13, 14].

Titanium nitride is deposited at different partial nitrogen pressures, from $3 \cdot 10^{-3}$ to 1 Pa (Table 3). This range of nitrogen pressures was selected based on literature sources [13, 15].

After coating, the surface microstructure of the obtained coatings and their microhardness were investigated (Table 4).

Coatings obtained at different nitrogen pressures differ in the amount and size of the droplet phase. The largest amount of droplet phase containing α-Ti is observed in coatings obtained at nitrogen pressures of $3 \cdot 10^{-3}$ Pa, $3 \cdot 10^{-2}$ Pa (Fig. 2, a, 2, b). They have a gray and yellowish-gray color. With an increase in nitrogen pressure to 1 Pa, the coatings acquire a brown-golden color, the amount of droplet phase on the surface noticeably decreases (Fig. 2, d).

The highest microhardness is observed in coatings obtained under nitrogen pressures of $3 \cdot 10^{-3}$ Pa, $3 \cdot 10^{-2}$ Pa (up to 26 GPa). With increasing pressure, the microhardness decreases and at a pressure of 1 Pa it is 18 GPa. Laboratory tests on thermal endurance of samples with coatings applied at different nitrogen pressures showed that the largest number of cycles are withstood by samples with titanium nitride coating obtained at a pressure of 1 Pa. Under pressures of $3 \cdot 10^{-3}$ Pa, $3 \cdot 10^{-2}$ Pa, along with the highest microhardness, an increase in the width of diffraction maxima (333) is also observed near the coatings, which characterize the microdistortion of the crystal lattice of chemical compounds contained in the coatings. This is probably explained by the introduction of nitrogen atoms, the diameter of which is larger than the diameter of a sphere inscribed in the titanium lattice [16]. High hardness and high level of microdistortions lead to increased fragility of the coating, which causes rapid destruction under the action of alternating voltage and technical impacts. The presence of a significant amount of droplet phase on the surface makes the destruction process intense. Increasing nitrogen pressure ($4 \cdot 10^{-1}$ Pa, 1 Pa) significantly reduces the level of microdistortions of crystal lattices in the coating, increasing its plasticity [8]. In this regard, the fragility

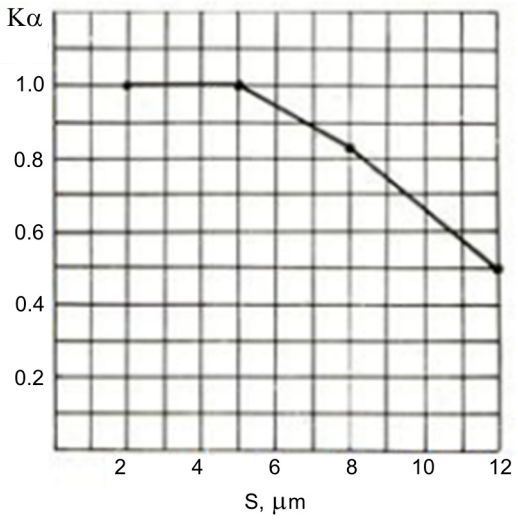

Fig. 3. Effect of coating thickness S on adhesion Kα

of the coating decreases with a sufficiently high hardness.

The titanium nitride coating obtained under a nitrogen pressure of 1 Pa provides the highest thermal endurance of the studied steels (Table 4). Another important parameter is the temperature of the working surface during ion bombardment, because the energy of ions during the bombardment process is significantly higher than the energy of ions in the case of condensation of the coating [9]. According to the technical specifications, the temperature of the substrate surface in the chamber of the Bulat-10 installation during ion bombardment varied from 300 to 800 °C. Temperature control was carried out using a reference sample with a chromel-alumel thermocouple mounted in it, which measures the temperature of the deposition surface. Ion bombardment has the most favorable effect on the substrate made of steels 4X5MFS and 5XNM at its temperature of 500 °C, which corresponds to the best adhesion of the coating to the substrate.

At lower temperatures, there is a tendency for the adhesion of the coating to decrease, which is accompanied by its peeling (Fig. 3, Fig. 4).

The material on which the coating is applied must be reliably protected from external factors due to increased hardness, corrosion and scale resistance. But at the same time, the probability of the appearance of such dangerous defects on the coating as macro- and micropores, microcracks, which can accelerate the destruction of the coating increases. Therefore, the thickness of the coating is a parameter that must be

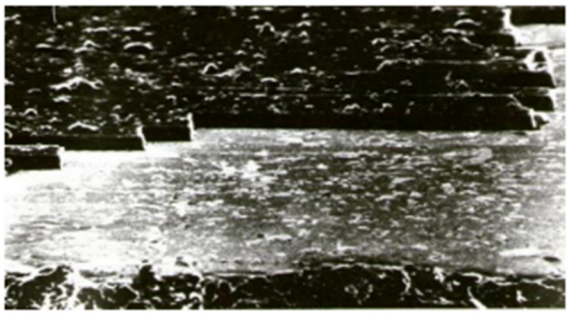

Fig. 4. Initial stage of peeling of a coating with a thickness of 8 microns, ×1000

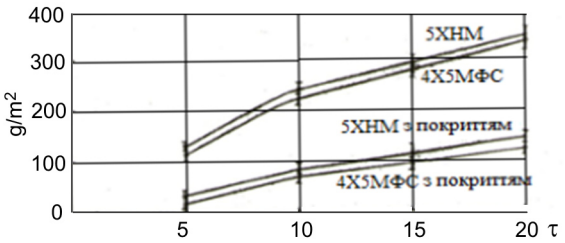

Fig. 5. Scale resistance of steels depending on time τ(h) 4X5MFS, 5XNM

optimized in each specific case [9, 16–18]. To determine the optimal thickness of the coating, which ensures its strong adhesion to the working surface of parts made of steel grades 4X5MFS and 5XNM, the dependence of the strength of the coating-substrate connection on the coating thickness was studied (Fig. 3). The best adhesion is achieved with coatings 2–5 μm thick. If the coating is more than 5 μm thick, its flaky delamination occurs (Fig. 4).

In the process of determining the scale resistance of a coated material, its protective properties can be judged by its significant indicators. The scale resistance of steels after heat treatment without coating and after applying a titanium nitride coating is shown in Fig. 5. The results indicate a strong influence of the coating on the oxidation resistance of steels 4X5MFS, 5XNM: after just 10 hours of operation, the weight gain in the coated steel is three times less than in the uncoated samples.

The corrosion resistance of samples of 4X5MFS and 5XNM steels with and without titanium nitride coating was tested. The tests were carried out in water at a temperature of 20 °C for τ=1000 h. The corrosion rate initially during interaction with the aqueous medium (the first 24 h) is high in both materials under study, although it is noticeable that the corrosion rate index in coated samples increases more slowly. This dependence occurs in the first 24 h. Then a significant decrease in the

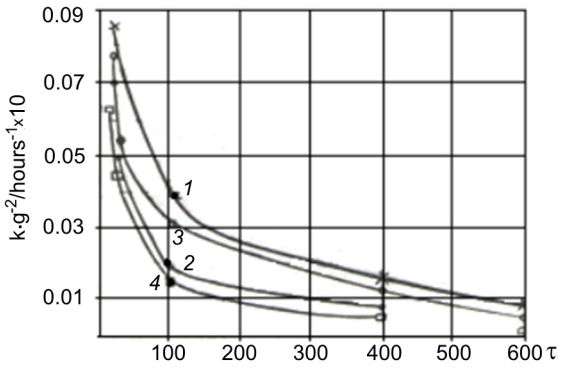

Fig. 6. Dependence of the corrosion rate index Z of steels 4X5MFS, 5XNM on the test time (h): 1 – steel 5XNM; 2 – steel 5XNM with titanium nitride coating; 3 – steel 4X5MFS; 4 – steel 4X5MFS with titanium nitride coating

corrosion rate index is observed. In the future, the corrosion rate index stabilizes and subsequently only slowly decreases (Fig. 6).

As laboratory tests have shown, a titanium nitride coating applied under optimal technological parameters provides a threefold increase in the corrosion resistance of the studied steels to which it is applied, and a two- to fourfold increase in scale resistance .

5. Conclusions

Summarizing the results obtained, we can conclude that a significant increase in the thermal endurance of 4Kh5MFS and 5KhNM steels is achieved by heating the substrate surface during ion bombardment to high temperatures, but not higher than the tempering temperature of these materials. In the case of ensuring good adhesion of the coating to the substrate and subsequent condensation on this heated surface of a coating with a minimum content of the droplet phase at a temperature of 500 °C and at a partial nitrogen pressure of 1 Pa, an increase in the corrosion resistance of the studied steels is ensured by three times, and scale resistance by two to four times.

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