



ICTE in Transportation and Logistics 2018 (ICTE 2018)

Application of chemical-thermal treatment for hardening of sprayed with supersonic coatings

Serik Nurakov^{a,*}, Marat Belotserkovsky^b, Tynys Suleimenov^a, Kurmet Aitlessov^a

^aEurasian National University named after L.N. Gumilyov, Satpayev 2, Astana, KZ-010008, Kazakhstan

^bBelarusian National Technical University, Independence 65, Minsk, BY-220007, Belarus

Abstract

In the global economy there is a significant increase in the scale of traffic, the implementation of which directly depends on the quality of transport equipment. Therefore, the work considers new technologies for hardening by modifying the working surfaces of parts of transport machines. The most effective ion-beam nitriding and thermodiffusion carbonitriding were selected for the modification of sputtered steel coatings. Experiments have shown that as the temperature of the nitriding process increases, the depth of the modified layer increases, and the microhardness of the layer also increases. The main phases are nitrides. The increased wear resistance of the nitrated layer is revealed. Carbonation leads to the formation of a modified layer with a thickness of 150-200 μm and a microhardness of 6500-7000 MPa. The main phase is carbonitrides. To regulate the depth and hardness of the layer, the technology of nitrocarburization has been changed by increasing the temperature and changing the composition of the medium. High adhesion strength was obtained.

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Peer review under responsibility of the scientific committee of the ICTE in Transportation and Logistics 2018 (ICTE2018).

Keyword: Transport equipment; Ion-beam nitriding; Microhardness; Adhesion strength

1. Introduction

The service life and quality of transport equipment used for transportation depend on the technology of their manufacture and operating conditions. In this regard, the article focuses on such an important problem as improving

* Corresponding author. Tel.: +7(701)-513-70-24; fax: +7-717-270-9457.

E-mail address: enuter@yandex.kz

the wear resistance of the working surfaces of parts of transport machines with new chemical-thermal methods. Methods to improve the quality of sprayed coatings by subsequent chemical-thermal treatment are easily realized in practice [1]. Among the large number of technologies for diffusion doping of the upper layers, the methods of nitriding are technologically distinct, environmentally safe and cost-effective [2], therefore ion-beam nitriding and diffusion carbonitriding were chosen for the subsequent modification of sprayed steel coatings.

2. The theoretical basis of the research method

An assessment was made of the possibility of improving the quality of gas-flame coatings by subsequent ion-beam implantation with nitrogen [3, 4]. In addition to flame spraying of wires, the ADM-10 hypersonic metallization was used. Ion-beam treatment of coatings obtained by spraying wires from martensitic steels (40X13, 95X18), ferritic (S-08G2C), and austenitic (X18H10T, 12X18H10T) classes was carried out using an ion source with closed electron drift. The source generated a band-type nitrogen beam 120 mm long and 2.5 mm wide. Implantation was carried out for two hours at ion energy of 1-3 kV and an ion current density of 2 mA / cm². The temperature of the samples during the ion-beam treatment varied from 600 to 800 K.

3. The results of the application of chemical heat treatment

The microhardness data are given in Table 1. The results of studying the microhardness and structural parameters and the phase composition of ion-modified coatings according to different regimes are given in Tables 2-4.

Table 1. Influence of the temperature of ion-beam nitriding on the microhardness of modified coatings.

Coating material	Microhardness (GPa) at different nitriding temperatures (K)						
	600	620	650	670	700	720	770
Martensite steels	8,6	11,3	12,9	14,0	15,9	12,7	11,3
Austenitic steels	5,6	6,2	8,0	8,9	11,1	12,0	11,8

According to the obtained data, as the temperature of ion-beam nitriding of coatings increases, the depth of the modified layer increases (up to 40 μm). The microhardness of the modified layer is thereby substantially increased and, as a result of the treatment, reaches the level of maximum values at 670-720 K (14000-15900 MPa). The main phases present in nitrogen-modified layers on martensitic grade steel coatings are ϵ - $(\text{Fe}, \text{Cr})_3\text{N}$ and $\gamma^1\text{-Fe}_4\text{N}$ nitrides.

Table 2. Structural parameters of modified coatings of martensitic grade steel.

Processing mode		Layer thickness, microns	Phase composition
GPN	N ⁺ 620 K	5-10	$\alpha\text{-Fe}, \gamma\text{-Fe}, \gamma^1\text{N}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}$
	N ⁺ 627 K	10-20	$\alpha\text{-Fe}, \gamma\text{-Fe}, \gamma^1\text{N}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}, \alpha^{11}\text{-(Fe, Cr)}_8\text{N}$ and $\gamma^1\text{-Fe}_4\text{N}$
	N ⁺ 720 K	15-25	$\alpha\text{-Fe}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}, \gamma^1\text{-Fe}_4\text{N}, \text{CrN}$
	N ⁺ 770 K	25-30	$\alpha\text{-Fe}, \text{Fe}_3\text{O}_4, \gamma^1\text{-Fe}_4\text{N}, \text{CrN}$
GM	N ⁺ 620 K	5-10	$\alpha\text{-Fe}, \gamma\text{-Fe}, \gamma^1\text{N}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}$
	N ⁺ 627 K	10-20	$\alpha\text{-Fe}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}, \gamma^1\text{-Fe}_4\text{N}$
	N ⁺ 720 K	15-25	$\alpha\text{-Fe}, \text{Fe}_3\text{O}_4, \epsilon\text{-(Fe, Cr)}_3\text{N}, \gamma^1\text{-Fe}_4\text{N}, \text{CrN}$
	N ⁺ 770 K	25-30	$\alpha\text{-Fe}, \text{Fe}_3\text{O}_4, \gamma^1\text{-Fe}_4\text{N}, \text{CrN}$

After ion treatment at temperatures of 720 and 770 K, a sharp decrease in the content of high-nitrogen ϵ -nitride and formation of CrN nitride is recorded in the nitrided layers, while the microhardness of the layer decreases to 11300-12700 MPa. In nitrogen-modified layers, oxide Fe_3O_4 is retained and oxide FeO is reduced.

Ion nitriding of gas-thermal coatings from austenitic steels results in the formation of modified layers with a thickness of 3-5 to 15-25 μm (Table 3). The microhardness of the nitrogen-modified layers on the GM and GPN coatings is (Table 1) from 5,600 to 12,000 MPa. The hardness of the unimplanted core of the sputtered 12X18H10T steel layers remains at the level of the initial values. Investigation of the microtopography of the surface layers after ion-beam nitriding has shown that the porosity of the coatings adversely affects the quality of the surface formed by

nitrogen ions hardened. It has been established that on the previously ground layers with a porosity of more than 7%, after ion hardening, on the surface of a third of the samples, areas of swelling (bloating) of a coating with a size of up to 200-500 μm appear.

Table 3. Structural parameters of modified coatings from steels of austenitic class.

Processing mode		Layer thickness, microns	Phase composition
GPN	N ⁺ 620 K	3-5	α -Fe, γ -Fe, Fe ₃ O ₄ , γ _N
	N ⁺ 627 K	5-10	α -Fe, γ -Fe, Fe ₃ O ₄ , γ _N ¹
	N ⁺ 720 K	10-15	α -Fe, γ -Fe, Fe ₃ O ₄ , γ _N ¹ , γ ¹ -Fe ₄ N, CrN
	N ⁺ 770 K	15-20	α -Fe, γ -Fe, Fe ₃ O ₄ , γ ¹ -Fe ₄ N, CrN
GM	N ⁺ 620 K	3-5	α -Fe, γ -Fe, γ _N
	N ⁺ 627 K	5-10	α -Fe, Fe ₃ O ₄ , γ _N ¹
	N ⁺ 720 K	10-15	α -Fe, γ -Fe, Fe ₃ O ₄ , γ _N ¹ , γ ¹ -Fe ₄ N, CrN
	N ⁺ 770 K	15-20	α -Fe, γ -Fe, Fe ₃ O ₄ , γ ¹ -Fe ₄ N, CrN

After peeling, the areas of swelling become cavities. Similar defects are observed when cast steels with surface microcracks are hardened. Obviously, the more developed the porosity of the layers, the stronger the effect of swelling. The conducted studies show (see Table 4) that at a layer density of more than 95% this effect does not occur.

Table 4. Results of the topography study of the surface of layers after ion-beam nitriding at a temperature of 680 K.

Method of layer spraying	Sprayable material (steel grade)	Porosity of the layer, %	Microtopography of the surface
GPN	Ferritic steels	≈10	Swelling
		≥8	Swelling
GM		≈4	Smooth without changes
		≈4	Smooth without changes
GPN	Martensite steels	≈10	Swelling
		≥8	Swelling
GM		≈5	Smooth without changes
		≈4	Smooth without changes

Nitriding of coatings from steel X18H10T at 600-620 K, leading to the formation of a modified gradient layer with a thickness of 3-5 μm , is not accompanied by an increase in the wear resistance of the steel surface under conditions of frictional contact interaction without lubrication. When transitioning to higher temperatures (670, 720 and 770 K), the wear resistance of the layer nitrided at 770 K is due to its great depth and high microhardness.

Carbonation of coatings was carried out in a container with a fuse in a mixture of powders containing a mass fraction of Al₂O₃ – 18, Cr₂O₃ – 72, C – 3, K₄Fe(CN)₆ – 5, NaHCO₃ – 2, at a temperature of 920 K for 4 hours. After chemical-thermal treatment, samples were taken together with the container to room temperature.

Saturation of carbon-nitrogen coatings from low-alloyed steel S-08G2S at selected modes leads to the formation of a modified surface layer with a thickness of 150-200 μm (see Fig. 1) and microhardness of 6500-7000 MPa (see Fig. 2). The main phase contained in the modified layer is carbonitrides with the crystal lattice of cementite Fe₃(C, N). The presence of iron oxides in the carbonitriding layer is not recorded, which indicates the reduction of FeO oxide during saturation. The metallographic analysis also indicates the dissolution of oxide films during the carbonitriding of the coating.

It was noted that the layer modified by carbon and nitrogen has a nonuniform thickness, nitrocellulose sections in the form of interlayers are found in the depth of the coating and on the boundary with the substrate. The indicated morphology of the modified interlayers in the depth of the deposited layers indicates a boundary mechanism for the diffusion of interstitial atoms in low-alloyed C-08 coatings.

Carbon-nitrided layers on 40X13 steel coatings obtained with the same regimes had a thickness of 100-120 μm and a microhardness of 7500-7700 MPa. The phase composition of the modified layer includes carbonitrides with the crystal lattice of cementite Fe₃(C, N), and also oxide Fe₃O₄.

The results of the metallographic analysis also indicate the preservation of oxide films in the modified coating of steel 40X13. If during the carbonitriding of coatings from low-alloyed steel S-08, the oxides FeO and Fe₃O₄ are reduced, then in the coatings of steel 40X13, the increased stability of the oxide Fe₃O₄ is noted, which is due to the high chromium concentration, therefore, the interlayers of chromium-doped Fe₃O₄ oxide in these regimes are not restored in the process of carbonitriding [5, 6].

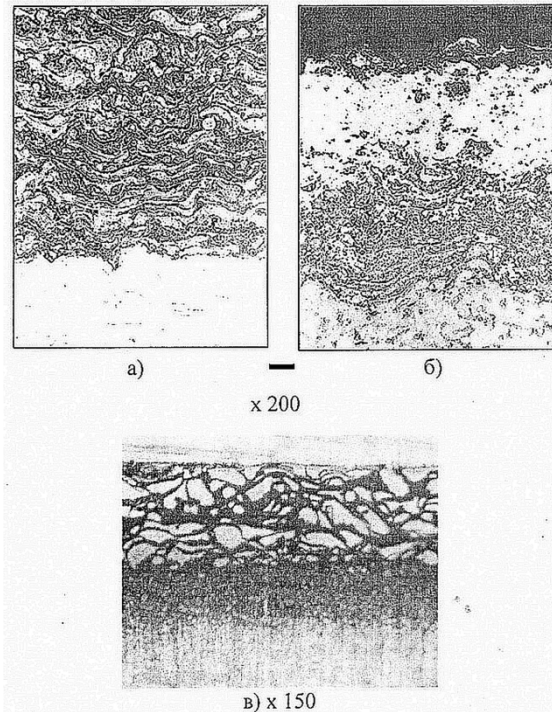


Fig. 1. Microstructure of carbonitrided steel coatings: (a, b) coatings of steel Sv-08G2S; (b) - a covering from steel 40X13.

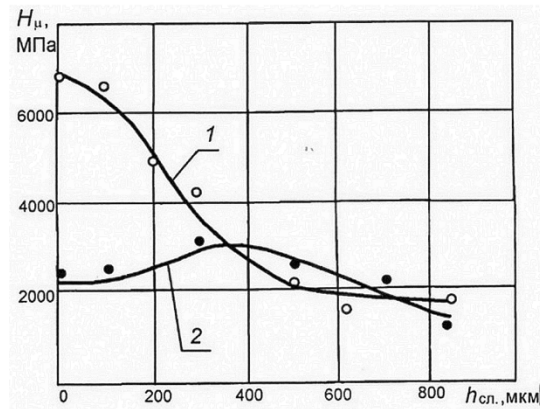


Fig. 2. Distribution of microhardness according to the depth of modified coatings of steel Sv-08G2S: 1 - coating after carbonitriding; 2 - initial state of the coating.

It is known [2] that by changing the temperature of the process, as well as the ratio of the potentials of carbon and nitrogen, it is possible to control the depth of the diffusion layer and its hardness. Therefore, it was proposed to change the technology of nitrocarburization, increasing the temperature to 1070 K and changing the composition of the saturating medium.

The depth of the diffusion layer, Y can be calculated by the formula [7].

$$Y = 2\Delta\sqrt{D\tau} \tag{1}$$

where D - diffusion coefficient;
 τ - process time, c;
 Δ - Dirac function, characterizing the point mass.

Investigation of the adhesion strength of coatings showed that the chemical-thermal treatment can significantly increase the adhesion (see Table 5). The increase in bond strength is characteristic for gas-flame wire coatings having a porosity in the range of 5-14%, and further increase in porosity leads to a decrease in adhesion. The increase in adhesion in carbonitrided coatings is due to the development of diffusion processes at the boundary between the coating and the substrate, the reduction of oxides on the substrate surface, the relaxation of internal stresses in the coating.

Table 5. Effect of porosity on the adhesion strength of carbonitrided coatings (without application of a sublayer).

Coating material	Adhesion strength (MPa) for different porosity (%)					
	≤4	5-9	7-10	10-14	12-16	13-17
Sv-08G2S	38	49	61	53	40	36
Pace. XTO 920 K 40X13	37	43	55	47	43	35
Pace. XTO 920 K 40X13	41	55	67	63	50	39
Pace. XTO 1070 K						

4. Conclusion

Thus, it is advisable to provide high wear resistance, hardness and other surface properties of coatings from alloys based on iron by such activation methods as chemical-thermal treatment. Using a combination of methods of supersonic sputtering and subsequent hardening opens up great opportunities in creating composite coatings with special properties. Such a combined technology does not require additional expensive equipment and operations, which predetermines the cost reduction of hardening and recovery processes.

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Serik Nurakov, doctor of technical sciences, professor, director of research laboratories at the Eurasian National University named after L.N. Gumilyov, Astana, Republic of Kazakhstan. He has more than 370 publications: patents, monographs, textbooks and teaching aids, standards, SSaRs, including abroad. Head of a number of scientific and technical projects. The field of scientific activity is mechanical engineering, technical service, construction, standardization. Contact information: 2 Satpayev str., Astana, Kazakhstan. Tel.: +7(701)-513-70-24. Contact him at enuter@yandex.kz.