ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1053–1060. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © S.A. Muboyadzhyan, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 1, pp. 103–109.

Erosion-Resistant Metal Nitride Coatings and Carbide and Their Plasmochemical Synthesis

S. A. Muboyadzhyan

All-Russian Scientific Research Institute of Aviation Materials Federal State Unitary Enterprise, State Research Center of the Russian Federation (RIAM), ul. Radio 17, Moscow, 105005 Russia
e-mail: mubo@mail.ru

Received December 1, 2009

Abstract—The influence of ion-plasma coatings made from high-hardness metal compounds on the erosion and corrosion resistance and mechanical properties of the alloy (substrate) + coating system is studied. The influence of the thickness, composition, and design of coatings based on metal nitrides and carbides on the relative gas-abrasive wear resistance of alloy+coating compositions in a gas-abrasive flux of quartz sand is discussed. It is shown that the zirconium nitride coating provides the best protection for compressor blades made of titanium alloys, without any decrease in fatigue resistance of the alloys, and chromium carbide coating is the most appropriate protection for steel compressor blades.

DOI: 10.1134/S1070363211050409

INTRODUCTION

Development and production of high-efficiency materials and coatings with special properties is one of the urgent problems in modern technics. The potential of conventional methods of low-temperature chemistry and metallurgy in this field is restricted by the highest attainable temperature level and particle energies, as well as the laws of equilibrium thermodynamics. Plasma methods open up radically new perspectives for materials production. The potential of known methods of the "atmospheric" plasma technology is also restricted in view of the fact that they make use exclusively of "gaseous" low-temperature plasmas with a low particle energy (<1 eV), where plasma is used largely as a heating source [1].

Vacuum plasma technologies ensure a high purity, which is of primary importance for most technologies of production of functional materials. Therewith, broad possibilities arise for generation of solid plasmas and their acceleration to required energies so that to produce materials by plasma condensation. In this case, other parameters, specifically high temperature, high degree of substance ionization, and the possibility of widely varying the energy of particles interacting with the support acquire a key importance. The important role here belongs to the chemistry of a new type, specifically non-equilibrium high-energy plasma chemistry, where many known chemical reactions are sharply accelerated and new types of reactions leading to compounds with unusual compositions and properties become possible. Mixing a number of active plasmas opens up possibilities for plasmochemical direct synthesis of complex substances from elemental plasmas (reactions without by-product formation).

Specific Features of Coating Formation from the Plasma Phase

Of key importance in the formation of materials by plasma condensation is the energy of condensing particles, a parameter which controls the efficiency of cleaning the surface under treatment by ion bombardment, adhesion of the condensate, and the structure of the resulting condensates. By varying the particle energy during condensation one can produce the same material in different structural modifications: from amorphous to crystalline; therewith, the shape and dimensions of crystals and their texture depend on the energy of particles interacting with the support [1, 2].

The processes that occur on the surface of a current-conducting support under a flux of metal plasma depend on the negative potential of the support with respect to the plasma (shift voltage). The support potential determines the energy of plasma ions

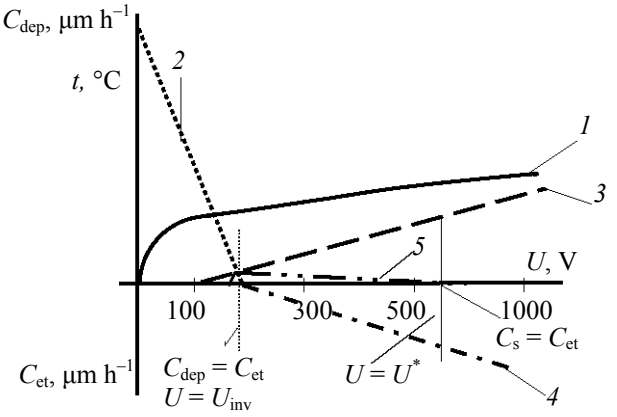

Fig. 1. Effect of shift voltage on the rate of ion treatment of the metal surface: (*1*) support temperature; (*2*) deposition rate C_{dep}; (*3*) saturation rate; (*4*) rate of ion etching C_{et}; and (*5*) rate of diffusion layer growth C_d.

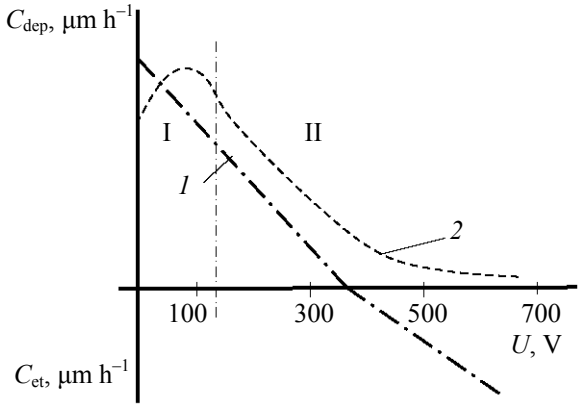

Fig. 2. Effect of shift voltage on the rate of ion treatment of the metal surface: (*1*) high-vacuum treatment and *(2*) plasmo-chemical treatment in a reactive gas medium.

interacting with the support surface. Plasma flux induces a number of interrelated processes on the support surface, specifically particle condensation with transfer the kinetic and potential energy of ions and neutral particles, ion and electron heating of the support, ion (cathode) sputtering and thermal diffusion saturation of the surface, implantation ("cold" surface saturation), melting, and vaporization of the surface layer of the support [3, 4].

At shift voltages of 200–1000 V and ion current densities of about 10–20 mA cm^{-2}, vigorous ion heating, ion etching (cathode sputtering), and ion thermal diffusion saturation occur on the support surface. The influence of shift voltage (U) on surface processes is shown in Fig. 1 [4].

When $U < U_{inv}$, ion condensation accompanied by condensate ion etching take place. Simultaneously ion heating of the support occurs. In the case of a pure metal plasma, support temperature (T_s) is related to shift voltage U by the following equation:

$$T_s = [J_i(U + U^{**})\varepsilon\sigma]1^{/4},$$

where σ is the Stefan–Boltzmann constant; $J_i = I_i/S$ (I_i is ion current and S, support surface area); U^{**}, volt equivalent the energy of interaction of the two-phase plasma flux with support [5], and ε, support emissivity. At $U = U_{inv}$, the condensate growth rate is zero, and coating condensation gives way to support ion etching (inversion). The etching rate (C_{et}) increases with increasing shift rate and, therewith, the rate of thermally induced ion saturation of the support surface (C_s) also increases. Depending on these rates, either ion heating and, primarily, ion etching ($C_{et} > C_s$) or surface ion saturation (modification) occur ($C_s > C_{et}$). When $U \geq U^*$ and $C_s \leq C_{et}$, the prevailing process is surface ion etching. Therefore, depending on the support material, ion type (pure metal or alloy ions), and shift voltage on the support (determines the ion energy), condensation, ion saturation, or ion etching accompanied by heating is the prevailing surface process [4].

Surface Processes on Plasma Treatment

Ion surface treatment of nickel heat-resistant alloys (HRA) and EI961, EP866, and other structural steels used in turbine blades and gas turbine engine (GDT) compressors, in pure metal plasmas (Cr, Al, Ti, Zr) over the entire range of shift voltages (200–800 V) on a support resulted in ion etching of the alloy surface at a rate of up to ~ 20 μm h^{-1}.

Metallographic analysis of the surface layers of the alloy and steel samples showed that surface etching is accompanied by vigorous diffusion of aluminum, titanium, and zirconium into the alloys and steels (the $U_{inv} < U < U^*$ range in Fig. 1). After 30-min treatment with with titanium ions of the ZhS26 heat-resistant alloy at the shift voltage 500 V, a ~ 20-μm diffusion layer containing 18–19 wt % of titanium in the subsurface layer is formed. After ion treatment in an Al plasma for 30 min, on the surface of the ZhS26 alloy we observed a characteristic transition diffusion layer on the basis of a Ni_3Al phase and carbides (~15–20 μm in thickness) and a thin interlayer (3-μm) of a NiAl phase (β-phase), which, too, suggests that the process occurs at $U_{Al} < U^*$ and the diffusion is reactive

in nature [6]. Surface ion modification of structural material parts allows one to affect the structural and phase state of the surface and, consequently, the properties of such materials, associated with the state of the surface (heat, corrosion, and fatigue resistance, etc.) [3, 4]. To form on the above-listed materials doped layers more than 10 μm in thickness, their surface ion modification was performed at temperatures no higher than 600 C to prevent overheating and softening of the support.

The processes on the surface of current-conducting supports in a metal-plasma flux in a reactive gas medium (N_2, C_2H_2, O_2) in a vacuum of 0.1–1 Pa, too, were largely controlled by the negative potential of the support with respect to plasma. But here, along with the above-mentioned processes, direct synthesis of metal compounds (nitrides, carbides, oxides, or their mixtures, depending on the composition and pressure of the reactive gas) took place on the support. At a stoichiometric ratio of the high-energy metal ion flux and gas flux, the corresponding stoichiometric metal compound is formed. In other cases, the process forms either a "metal + metal compound" composite coating (low gas pressure) or an overstoichiometric metal compound (high gas pressure). Therewith, the characteristic dependence of treatment or specific weight change rate on shift voltage look like that shown in Fig. 2.

The rate of high-vacuum deposition and ion etching for a pure Group IVB–VIB metal on a support of the same metal continuously decreases with increasing U. This is explained by the lack of structural and phase transformation on the support surface. Group IVB-VIB metals have high U_{inv} values (usually above 400 V), whereas the U_{inv} values of Ni and Co alloys span the range ~180–200 V.

When a reactive gas is fed to the vacuum chamber, the rate of metal compound deposition C_{dep} changes, and the $C_{dep} = f(U)$ function takes the shape of curve *2* in Fig. 2. Therewith, the function has two characteristic portions. Portion I (0–~150 V), when ions have a fairly low energy, and the support has a low temperature. Here the support temperature increases with increasing U, and the corresponding metal compound starts to form on the surface. Therefore, the deposition rate increases, and, with further increase of U, ion etching initiates, while ion saturation (modification) of the support is virtually suppressed. The second portion of the curve (portion II) shows decrease of the deposition rate with increasing shift voltage, on account of the enhancing surface ion etching. Characteristically, most metal compounds (nitrides, carbides, carbonitrides, etc.) have $U_{inv} > 600$–800 V.

The plasmochemical synthesis of solid metal carbide and nitride coatings at high (up to 600 eV) particle energies was used to develop reinforcing coatings for protection of steel and titanium GTE compressor blades from dust erosion on exposure to gas-abrasive flux. The coatings were formed on a MAP commercial ion-plasma device [7–9].

The gas-abrasive wear of the surface depends on the physical and mechanical properties of the support or alloy–coating composition, temperature of the surface and its stress and deformation state, as well as conditions of interaction with the two-phase flux. The important parameters here are the attack angle (the angle between the velocity vector of the solid particle and the support surface), particle velocity, size, and shape, physical and mechanical characteristics of the abrasive material (hardness, impact strength), particle concentration in the flux, flux temperature, humidity, and pressure, as well as time of exposure to flux and the total number of abrasive particles per unit surface. Generalization of the available evidence shows that the gas-abrasive wear of GTE compressor blades occurs largely on the ground or near the ground and caused mostly by spherical (rounded) particles of quartz sand 100 μm in size.

Gas-abrasive wear affects the characteristics of GTE compressors, enhances aerodynamic losses, deteriorates efficiency of the compressor by increasing the radial split and changing the profile geometry and surface coarseness of compressor blade body, and also decreases the gas dynamic stability margin of the compressor.

Ion-Plasma Protective Coatings for Moving Compressor Parts

The RIAM has performed long-standing R&D works on ion-plasma erosion-protective coatings for steel and titanium GTE compressor [7, 8].

The erosion resistance of ion-plasma coatings was assessed by comparative tests on a special stand [8, 9]. The erosive medium was quartz sand from the Lubertsy sand pit (particle size ~300–350 μm, maximum size 700 μm). The particle velocity in the flux was ~80 m/s, erosive flux rate 200 ± 5 g min^{-1}, test time 6 min (3 cycles 2 min each). One side of a

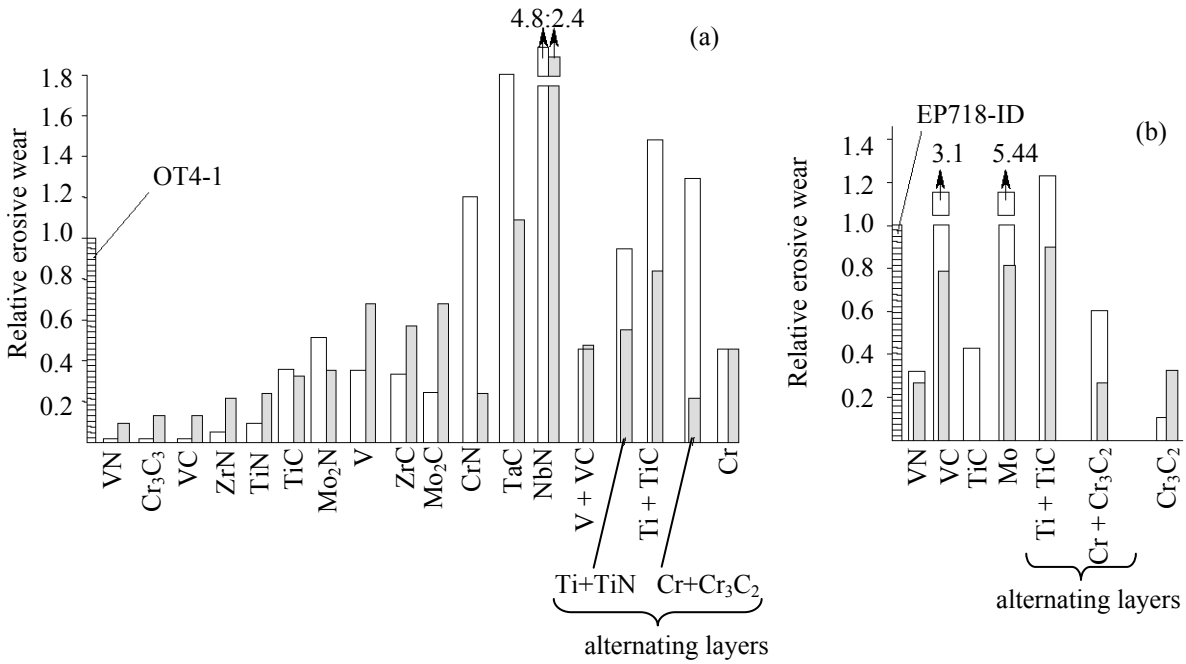

Fig. 3. Relative erosive wear (river sand, P = 3 atm) of metal nitride and carbide coatings, as well as multilayer compositions like Me+MeC(N) on the (a) OT4-1 and (b) EP718-ID alloys: ( ) no coating (the erosive wear of alloys is taken for 1; attack angle α = 20° and 70°); with coating at ( ) α = 70° and ( ) α = 20°.

plane 25×25-mm sample was exposed (the rare side was shielded from particles by the sample holder). The erosion entrainment of the material was estimated gravimetrically. The erosion resistance was assessed visually by means of a binocular microscope, as well as gravimetrically. At constant parameter of the dust and gas flux, the erosive wear depends exclusively on the coating material and the quantity of the consumed erosive medium. Tests were performed at two different orientations of the sample plane with respect to the incoming flux axis, attack angle α, deg: 70 (flow over like frontal impact) and 20 (tangent flow over).

Factors Responsible for Erosion Resistance of Coatings

In searching for an erosion-resistant material we tested a wide range of coatings: pure metals, alloys, and metal carbides and nitrides. The results of comparative erosion tests showed that the most promising class of materials which exhibit enhanced erosion resistance compared with their protected steels and titanium alloys is formed by solid coatings (H > 20 GPa) on the basis of metal carbides and nitrides.

Principal physical and engineering factors which affect the erosion resistance were revealed. It was found that the erosion resistance, apart from the properties of the material, is controlled by the characteristics of the support material, i.e. one should consider the erosion resistance of the support–coating composition, rather than the coating material alone. In this case, when optimizing coatings in terms of erosion resistance, one may well select different coatings for different types of materials (for example, titanium alloys and steels). Moreover, the erosion resistance is much affected by the thickness of the coating, its deposition mode, and quality of surface pretreatment.

Figure 3 presents the block diagrams of the relative erosive wear of a series of coatings for the titanium alloy OT4-1 and alloy EP718-ID. These data show that the titanium alloy is best protected by zirconium, vanadium, titanium nitrides and vanadium and chromium carbides, and the best coatings for the EP718-ID alloy are chromium and titanium carbides and vanadium nitride [8].

Figure 4 show the dependences of relative erosive wear on coating layer thickness for titanium alloy–ZrN and alloy–Cr_3C_2 compositions. As seen, the erosion resistance of the titanium alloy–ZrN system at the attack angle 70° appreciably decreases if the coating thickness gets below 15 μm [7, 8].

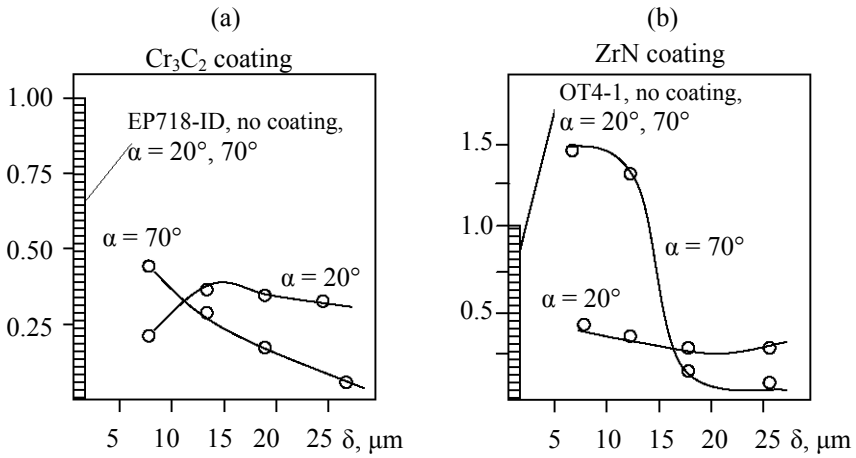

Fig. 4. Dependence of the relative erosive wear of the (a) EP718-ID+Cr_3C_2 and (b) OT4-1+ZrN compositions on coating thickness.

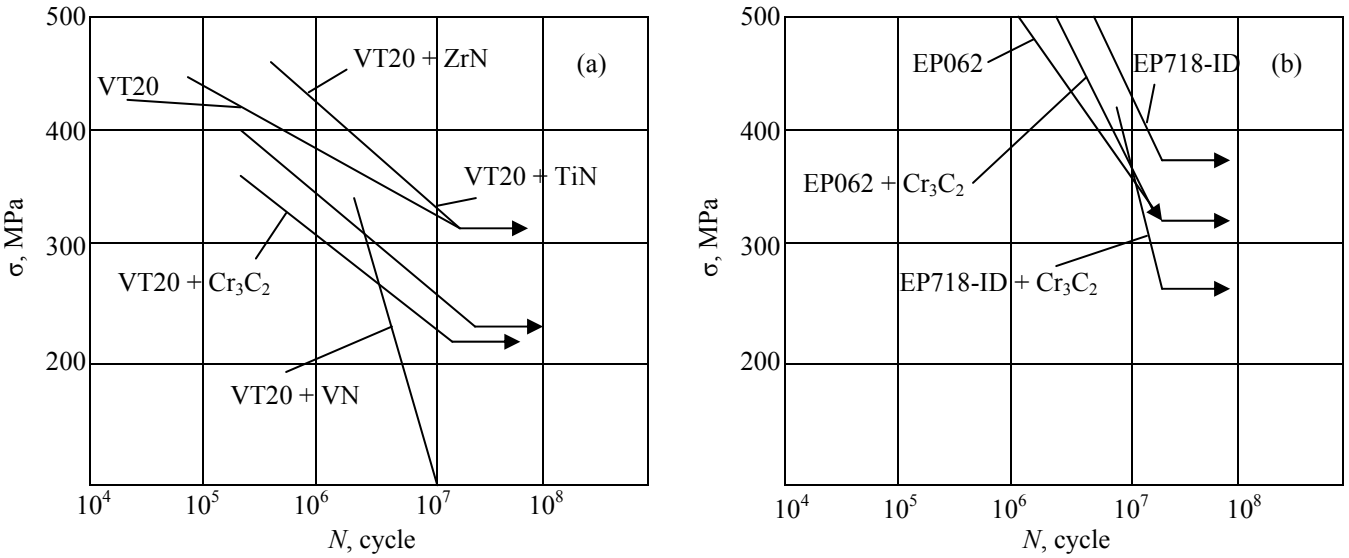

Fig. 5. Effect of coatings on the fatigue strength of the (a) VT20 alloy and (b) EP718-ID alloy and EI962 steel.

With the EP718-ID alloy, this effect is less pronounced, and the optimum coating thickness range here is 15–30 μm. Therewith, it should be mentioned that the ZrN coating thicker than 15 μm is at all impossible to obtain on the EP718-ID alloy, since the coating involves high residual stresses and tends to exfoliate on cooling.

The most resistant compositions, like ZrN-coated titanium alloy and Cr_3C_2-coated steel, were subjected to additional erosion stand tests at the RIAM at abrasive particle velocities of up to 250 m s^{-1}.

The test results provided evidence showing that these compositions are indeed highly resistant to erosion.

The corrosion resistance of erosion-resistant coatings on compressor materials (steels and titanium alloys) was assessed by tests in (I) tropical chamber; (II) salt mist chamber, (III) 3% aqueous NaCl; (IV) urban industrial environment; and by (V) express cyclic procedure at two temperatures: 500 and 700°C.

The VT20 and OT4-1 titanium alloys with TiN, ZrN, TiC, Cr_3C_2, VN, and VC coatings were subjected to tests I–III, and the EI962 and EP866 steels and EP718-ID allow with a Cr_3C_2 coating were subjected to tests I, II, IV, and V.

The tropical chamber was operated by the following program: 8 h at 50°C and humidity ψ =

Table 1. Effect of erosion-resistant coatings on the mechanic properties of the VT9 alloy

Coating type	σ, MPa	Long-term strength at 550°C	
		σ, MPa	time to rupture τ, h
No coating	697	560	4.5
		500	10.5
		400	80.5
		380	98.5; 161
Vanadium nitride, VN	722	400	83.5
		380	72
Zirconium nitride, ZrN_x	656	450	12
		380	91.5
Chromium carbide, Cr_3C_2	712	450	16
		400	82; 131
		390	213
		380	224

100%; 12 h at 20°C and ψ = 100%; 4 h at 20°C (drying). Express cyclic tests were performed by the following program: keeping at a specified temperature for 1 h; cooling in air for 1–2 min; cooling by immersing into a 3% solution of NaCl; keeping in a humid chamber for 22 h; a total of 10 cycles were performed. The tests in a tropical chamber were lasted 5–8 months, and the tests in a salt mist chamber, 3% NaCl, and urban industrial environment, by 5 months [7–9].

These tests gave worse results with vanadium nitride and carbide coatings on titanium alloy compositions, and, therewith, especially heavy erosion was observed in the presence of NaCl (salt mist chamber, 3% solution of NaCl). On the Cr_3C_2 coating we observed point corrosion after salt mist tests. Samples with other coatings showed no point corrosion or exfoliation in all corrosion tests.

The EI962 and EP866 steels and EP718-ID alloy coated with Cr_3C_2 acquired defects (either point corrosion or coating chips) after all corrosion tests in the presence of NaCl. Less pronounced defects develop upon long-term tests in industrial environment and are almost lacking in a tropical climate chamber.

The resulting data together allow the following conclusion: The TiN, TiC, Cr_3C_2, and ZrN_x coatings on titanium alloys and Cr_3C_2 coating on EI962 and EP866 steels and EP718-ID alloy fail to ensure protection in rigid marine conditions, but they exhibit a fair corrosion resistance in general climate conditions.

Assessment of the effect of coatings on the mechanical characteristics of their protected materials was performed by short- and long-term, as well as fatigue strength tests.

Table 2. Effect of erosion-resistant coatings on the properties of compressor blade materials

Parameter	Chromium carbode			Zirconium nitride		
Density, kg m^{-3}	6680			7090		
Microhardness H_μ, GPa	25–29			22—25		
Support material	EI962-Sh	EP718-ID	EP866-Sh	OT4-1	VT9	VT20
Working temperature, °C	up to 600	up to 700	up to 650	up to 500	up to 500	up to 550
Relative erosion resistance of uncoated material	1	1	1	1	1	1
with coating at α = 20°	8	4	11	9	–	8
with coating at α = 70°	19	8	25	30	–	25
Fatigue strength σ_{-1}[a] (at $N = 2\times10^7$ cycles)	320/320	380/280				32/32
Long-term strength[a], σ_{100}, MPa						
at 450°C	–	–	–	–	680/650	–
at 600°C	–	–	340/340	–	–	–

[a] In the numerator and denominator, data for uncoated and coated alloys are given, respectively.

The results of short- and long-term strength tests for the VT9 titanium alloy with different coatings are shown in Table 1. As seen from these data, the coatings have almost no effect on the tested characteristics of the protected material.

The results of fatigue strength tests (at 20°C) of steels and VT20 titanium alloy with different protective coatings (Fig. 5) revealed a strong dependence of the fatigue strength of alloy–coating compositions on the coating material. Thus, of the coatings tested with the titanium alloy, the ZrN coating showed a higher fatigue strength that the uncoated alloy. The other coatings, including TiN, have a lower fatigue strength than their protected alloy.

The fatigue strength of the EI962 steel with a Cr_3C_2 coating is equal to that of the steel with no coating. At the same time, the same coating decreases the fatigue strength of the EP718-ID steel from 380 to 280 MPa.

Our research results allow the following coatings to be recommended for protection from erosive wear: a ZrN ion-plasma coating for VT20, VT9, OT4-1, and other titanium alloys and a Cr_3C_2 coating for steels. Control fatigue strength tests are obligatory for each type of compressor blades. The effect of erosion-resistant coatings on the properties of compressor blade materials is shown in Table 2.

Summarizing the reported results, we can conclude that new technologies based on vacuum arc discharge, in particular, high-energy plasma chemistry, make it possible to form coatings or modified layers with high erosion and corrosion strengths on item surfaces. The RIAM has commercialized these technologies on the basis of MAP industrial installations, which provided essential quantitative and ecological advantages for the process of protection of steel and titanium blades and other GTE compressor parts from erosion and corrosion wear.

Along with that, the technology of deposition of erosion-resistant ZrN and Cr_3C_2 coating on MAP-1M, MAP-2, and MAP-3 installations was improved, which allowed enhancement of the protective properties of the coatings. The transfer to assisted deposition (assisted with argon ions with the energy of 30 keV, MAP-3 automated installation, RIAM design) changes the structural and phase state of the coating, improves its structure and thus enhances its erosion resistance. Samples of the OT4-1 titanium alloy with a ZrN coating with a <200> + <111> texture were obtained, which exhibited enhanced erosion resistance (from 0.1 to 0.04 and from 0.033 to 0.029 at the dust–air flux attack angles 20° and 70°, respectively) [9].

The work on improvement of erosion-resistant coatings are in progress and aimed at developing erosion- and corrosion-resistant coating for general climate applications. In this context, we consider two-layer nanostructured coatings containing a corrosion-resistant sublayer and a highly corrosion-resistant TiN, Cr_3C_2, ZrN, or other outer layer, as well as nanolayered coatings with alternating TiN/ZrN, TiAlN/ZrN, TiC/Cr_3C_2, AlN/TiN, and other layers (10–15 to 80 nm in thickness), applied on MAP installations [10]. The transfer to nanostructured and nanolayered compositions will allow reduction of residual stresses in the coating with simultaneous increase of its viscosity and hardness, which may enhance the erosion and corrosion resistance of reinforcing coatings for GTE compressor blades.

CONCLUSIONS

The use of vacuum arc discharge and high-energy plasma chemistry technologies (MAP-1M, MAP-2, and MAP-3 installations) allowed us to develop metal nitride and carbide protective ion-plasma coatings for GTE compressor parts, which are highly resistant to gas-abrasive wear.

Coatings of Cr_3C_2 on compressor steels and of ZrN on titanium alloys provide a fair corrosion resistance in general climate conditions, do not decrease the strength and fatigue strength of titanium alloys and steels, enhance up to 25 times the erosion resistance on tangent flow over of the surface with the dust–air flux (attack angle 20°) and up to 35 times at the attack angle 70° (by the results of tests for gas-abrasive wear), and makes possible exploitation of titanium and steel blades and other GTE compressor parts at 500 and 650°C.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 09-08-12162).

REFERENCES

1. Blinov, I.G., Dorodnov, A.M., Minaichev, V.E., Muboyadzhyan, S.A., et al., *Vakuumnye sil'notochnye plazmennye ustroistva i ikh primenenie v tekhnolo-*

gicheskom oborudovanii mikroelektroniki (Vacuum High-Current Plasma Devices and Their Application in the Engineering Equipment for Microelectronics), Moscow: TsNII "Electronika," 1974, part I, no. 7(268), p. 84; 1975, part II, no. 8(269), p. 75.

2. Dorodnov, A.M., *Fizika i primenenie plazmennykh uskoritelei* (Physics and Application of Plasma Accelerators), Morozov, A.I., Ed., Minsk: Nauka i Tekhnika, 1974, pp. 330–365.
3. Muboyadzhyan, S.A., Budinovskii, S.A., and Pomelov, Ya.A., in *Aviatsionnye materialy i tekhnologii. Vysokozharoprochnye materialy dlya sovremennykh i perspektivnykh gazoturbinnykh dvigatelei i progressivnye tekhnologii ikh proizvodstva* (Aviation Materials and Technologies. High-Heat-Resistance Materials for Present-Day and Perspective Technologies for Their Production), Moscow: RIAM, 2003, pp. 102–116.
4. Muboyadzhyan, S.A., *Konvers. Mashinostr*., 2004, no. 4, pp. 69–77.
5. Muboyadzhyan, S.A., *Metally*, 2008, no. 2, pp. 20–34.
6. Bokshtein, B.S., *Diffuziya v metallakh* (Diffusion in Metals), Moscow: Metallurgiya, 1978, p. 238.
7. Muboyadzhyan, S.A. and Pomelov, Ya.A., *Vopr. Aviats. Nauki Tekh. Aviats. Mater*., 1992, no. 1, pp. 58–66.
8. Muboyadzhyan, S.A. and Pomelov, Ya.A., in *Aviatsionnye materialy i tekhnologii. Vysokozharoprochnye materialy dlya sovremennykh i perspektivnykh gazoturbinnykh dvigatelei i progressivnye tekhnologii ikh proizvodstva* (Aviation Materials and Technologies. High-Heat-Resistance Materials for Present-Day and Perspective Technologies for Their Production), Moscow: RIAM, 2003, pp. 116–131.
9. Muboyadzhyan, S.A., *Metally*, 2009, no. 3, pp. 3–20.
10. Kablov, E.N., Muboyadzhyan, S.A., and Lutsenko, A.N., *Vopr. Materialoved*., 2008, no. 2, pp. 175–186.