Influence of intermetallide coatings on the high-temperature corrosion resistance of martensite steel in various structural conditions

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Abstract. The effect of coatings deposited from a vacuum-arc plasma on the high-temperature corrosion resistance of martensitic steel in ultrafine-grained and coarse-grained state is studied. It is proved that coatings obtained from a vacuum-arc discharge plasma increase the high-temperature corrosion resistance of martensitic steel. The analysis of high-temperature corrosion resistance was carried out using the method of accelerated cyclic tests developed by the All-Russian Institute of Aviation Materials.

1. Introduction

In gas turbine engines (GTE), the most loaded parts are compressor blades and turbines. They work in conditions of high temperatures, aggressive environment and heavy loads. To improve the mechanical properties of GTE parts, it is perspective to use materials with ultrafine-grained structure (UFG) together with traditional materials with a coarse-grained structure (CG). However, materials with a UFG structure are subject to a higher corrosion rate compared to samples with a CG structure, this is due to a significant number of defects and the presence of a longer grain boundary, which are active centers of corrosion damage [1].

Thus, work is underway to develop new methods and coating processes in the direction of creating multi-layer composite coatings that allow increasing the life and reliability of the GTE parts [2].

Article [3] illustrated the corrosion properties of Ti-Al-N / Ti-Al two-layer coating deposited by magnetron sputtering on magnesium alloy AZ31 are presented. Coatings were produced by spraying composite Ti / Al composite targets. Corrosion tests were carried out in an aqueous solution of 3.5% NaCl. The result showed that the coating effectively works in aggressive environments.

In the work [4], the authors of A.M. Smyslov, A.D. Mingazhev and others consider the possibility of obtaining vacuum-plasma nanolayer coatings for blades of turbomachines made of titanium alloys by combining the processes of electric arc deposition and ion implantation. The vacuum-plasma deposition of a metal sublayer and nanolayers of aluminum nitrides, carbides and / or aluminum carbonitrides or titanium, zirconium and aluminum compounds with nitrogen and / or carbon is produced on the blade surface. Allowed to increase in comparison with the existing coating (ionic nitrogen implantation and stabilizing annealing, ion-plasma coating of titanium nitride is carried out after ion implantation) resistance to salt corrosion (up to 1.5 times), drip-shock erosion (up to 2.1
times), gas-abrasive erosion (by 2.5 times). Thus, research aimed at developing technology to increase the corrosion resistance of aviation materials is relevant.

Thereby, this article is devoted to the generalization and identification of the regularities of the corrosive behavior of various materials with the UFG structure with their CG analogs and the increase in their corrosion resistance at high temperatures by the deposition of coatings from the vacuum-arc discharge plasma.

2. Material and methods
As initial materials, were used samples of EI 961 stainless steel with a coarse and ultrafine-grained structure.

To form a UFG structure, samples with a diameter of 20 mm and a thickness of 1 mm were subjected to intense plastic deformation by torsion (IPDT) at a pressure of 6 GPa, with a speed of 10 turns.

The experiments were carried out on a modernized installation for vacuum ion-plasma deposition of NNV-6,6 I1. In the vacuum chamber, samples were installed from martensitic steel EI 961c CG and UFG structure. When the pressure in the chamber is \( P = 1.5-2 \times 10^{-3} \) Pa, the TiN coating was deposited on the first sample. The second sample was deposited with a multi-layer composite coating based on the intermetallics of the TiAl (TiAl N) system developed at the USATU laboratory. The third sample was nitrided at the first stage with a high-current plasma source with a cathode for 60 min, and a multilayer composite coating of the intermetallic system TiAl (TiAl N) was deposited in the second stage. The currents of the arc evaporators are set in the range \( I = 60-120 \) A, the current of the cathode is \( I_{\text{cal}} = 90-120 \) A, the arc discharge current of the plasma source is \( I_{\text{ugus}} = 40-60 \) A, the temperature of the part is \( t = 550 ^\circ \) C. Within 60 minutes the process of deposition of the multilayer composite coating of the TiAl / TiAlN and TiN system occurs.

Corrosion resistance tests were carried out according to RTM 1.2.189 - 2006 (VIAM) using the accelerated cyclic test method. During the course of this procedure, the samples with coatings are held for 1 hour at the test temperature in an atmospheric oven and then air-cold for 1-2 minutes and cooled in a 3\% NaCl solution to room temperature, then held for 22 hours in a wet desiccator. The duration of the test is 10 cycles.

3. Results and discussion
On samples of steel EI 961 with a CG structure with coatings, TiAlN and nitriding + TiAlN compositions provided better corrosion resistance. Specific change in the mass of samples coated with TiAlN, nitriding + TiAlN decreases in comparison with uncoated samples by 4 and 3 times. Researches on the corrosion resistance of TiN coated samples revealed that the specific gravity losses are \( 4.1353 \) g/m², which is 2 times lower than in the initial state. (Fig.1)
Visual inspection (Fig. 2) of the samples after 10 cycles of the accelerated cyclic corrosion tests (ACCT) at a temperature of 500 °C showed that the surface of the uncoated samples of EI961 steel is powdered with loose corrosion products. On samples with TiAlN coatings, nitriding + TiAlN, a partial coating peeling is seen, no corrosion uclers are detected. It is obvious that cracks arise and develop mainly along the grain boundaries of the matrix under the coating, while the coating deforms plastically, and cracks appear in it after they are formed in the matrix. It has been established that TiN coated samples have a coating peel of about 70%, small pittings with a diameter <0.1 mm.
Tests on the corrosion resistance of steel EI961 with UFG structure (Fig. 3) also revealed a decrease in the specific mass of samples with TiAlN coatings, with nitriding technology + TiAlN in 1.8 and 2.8 times compared with the initial samples. As a result of visual inspection (Fig. 2), samples with a TiN coating have a 80-90% coverage peeling, the remaining samples with TiAlN coatings, nitriding + TiAlN - about 10-20%. After the ACCT, the initial samples with the UFG structure are completely covered with corrosion products, and there are corrosive ulcers.

![Figure 3. Appearance of samples from steel EI 961 (UFG) before the tests: a) uncoated; b) coated with TiN; c) coated with TiAlN; d) coated with nitriding technology + TiAlN; After 10 ACCT cycles at a temperature of 500°C: e) uncoated; f) coated with TiN; g) coated with TiAlN; h) coated with nitriding technology + TiAlN.](image)

As seen from (Fig. 4a.), after the corrosion test the entire surface of the sample was subjected to continuous corrosion. On the surface of the sample ulcers formed, as well as the places of exfoliation of the material.

![Figure 4. Surface structure of UFG without coating after corrosion resistance test.](image)

(Fig. 4b) shows a sample coated with TiN after the corrosion test. As seen from the photo that the coating peeled off mainly along the edges of the sample, and one large piece has peeled closer to the middle of the sample. The peeled and corroded areas account for 37% of the total sample area.

(Fig 4c.) shows a sample coated with TiAlN after the corrosion test. As seen from the photo that the coating has peeled off mainly along the edges of the sample, and also there are several small areas in the middle of the sample. The peeled and corroded areas account for 22% of the total area of the sample.
Corrosive destruction of coatings having high chemical and thermal stability can be contributed by various disruptions in their structure. These include: pores, depressions, delamination, lamination, separation from the substrate, chips, cracks, submicrochannels between columnar crystals, scaly, droplets and sprays of hardened metal on the surface of coatings, uneven thickness. All these structural defects can cause, to varying degrees, accelerated local corrosion damage to the coatings.

4. Conclusions
The conducted researches of corrosion tests of martensitic steels with coarse-grained and ultrafine-grained structure allowed to establish that:
- The corrosion resistance of martensitic steels with a CG structure is 30% higher than that of the UFG structure, and therefore, when using martensitic steels with a UFG structure, the effect of the structure on high-temperature corrosion resistance should be taken into account.
- Deposition of TiAl3 / TiAlN protective coatings on the surface of martensitic steels makes it possible to increase the high-temperature corrosion resistance for materials with a short-circuit structure by a factor of 4, and for the UFG structure in 3 times;
- The introduction of ionic nitriding prior to the application of protective coatings allowed to improve the result of corrosion resistance only for materials with UFG structure (3.2 times).

References
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