Investigation of influence of structure and TiAl$_3$/TiAlN intermetallic coatings on the corrosion behavior of martensitic steels

E Vardanyan, K Ramazanov, I Yagafarov, A Khamzina, R Agzamov

Ufa State Aviation Technical University, Ufa - 450000, Russia

Email: vardanyaned@gmail.com

Abstract. The paper considers several approaches to protect martensitic steels with ultrafine-grain (UFG) structure in aggressive environments. Scanning electron microscopy was used to study the microstructure and composition of steel substrates and coatings. The samples were also subjected to corrosion tests. Regularities of corrosion behavior were specified for the UFG steels. The samples were subjected to ion nitriding in a glow discharge and deposition of protective TiAl$_3$/TiAlN coatings in vacuum arc discharge plasma. Corrosion rates were identified for different treatments.

1. Introduction

Recently, bulk nanostructured materials of the grain size of 100-300 nm with unique structures and properties were developed. The materials change such fundamental characteristics as the Debye and Curie temperature, saturation magnetization, etc. Currently, particular attention is given to the method of producing such materials and namely severe plastic deformation (SPD) because it allows creating high volume semi-finished nanostructured products in the form of bars, thin foils and wires for various applications. At the present time we also observe transition from laboratory SPD experiments to designing pilot industrial technology based on continuous processes [1,2].

Until now, great progress has been made in the development of physical principles that improve properties in the study of structural models and evolution upon annealing, the study of some fundamental deformation characteristics, namely, magnetic properties, elasticity, internal friction, grain boundary diffusion, etc. However, the issue of corrosion behavior of such materials remains understudied, as existing data are insignificant and contradictory.

Properties of nanocrystalline materials cannot be predicted from the properties of corresponding coarse-grain analogues. The imperfections of the crystal lattice in metals and alloys due to deformation and high defect ratio in grain-boundary areas contribute to a local increase in the velocity of dissolution of these zones, which ultimately leads to accelerated dissolution. Therefore, there is a need in approaches to improve resistance to corrosion of such materials, which include ion nitriding, ion-plasma coating, combined methods, passivation, oxidation, chemical and electrochemical polishing.

The study of corrosion properties for coatings with intermetallic phases (TiAl, TiAl$_3$) are given in [3-7]. Literature review showed that Ti-Al intermetallic coatings that contain TiAl$_3$+TiAl phases demonstrate good corrosion resistance and can be considered for the protection of UFG martensitic steel.
The aim of this work is to identify regularities in corrosion behavior of CG and UFG martensitic steel in relation to the type of its processing.

2. Experimental approach

Specimens of martensitic steel EI-961SH with coarse-grain and ultrafine-grain structure were used as experimental materials.

Samples of 20 mm in diameter and 1 mm thick were subjected to severe plastic deformation by torsion (SPDT) under the pressure of 6 GPa with 10 twists to produce the UFG structure.

Intermetallic Ti-Al coatings were applied in the installation NNV-6.6-I1. Samples of martensitic steel EI-961SH were placed in a vacuum chamber. Technological spraying regimes changed in the following ranges: chamber pressure P = 10^{-1}–10^{-2} Pa; arc current I = 60-120 A; processing time t = 60 min [9].

![Figure 1. Scheme of the experiment.](image)

Ion nitriding was carried out in a modernized installation ELU-5M. Argon and a mixture of nitrogen, argon, acetylene (N₂ 75% + Ar 20% + C₂H₂ 5%) were used as a working gas. The pressure of the working gas varied in the range of 5...200 Pa. [10].

Corrosion tests were carried out according to GOST 9.905-2007. The tests were performed in artificially created conditions that simulated climatic effects of the atmosphere; the corrosive medium was composed of 3% NaCl.

The conductivity of the solutions was measured with Dulcometer LFWS 1C2 with the cell constant of 1.0 cm⁻¹ and the measuring range of 10-200 *S/cm. The temperature was controlled automatically with the integrated potentiometer Pt 100. Conductivity was measured with a conductivity probe that was inserted into test solutions.

The Dulcometer was set up in the following order: a series of standard KCl solutions with known electrical conductivity was prepared; the probe was dipped into the electrolyte and conductivity was recorded using a special button after 3-5 min.; then the Dulcometer measured electrical conductivity of the test solution in the automatic mode.

Corrosion resistance was measured by gravimetry.

3. Results and discussion

The microstructure and elemental composition of the surface in UFG samples as well as the coating layers were investigated by scanning electron microscopy (Figure 2, Figure 3).

Table 1 shows the results of measuring the atomic ratio of the chemical elements in different points of the coating (Figure 3).

Analysis of the chemical composition showed the maximum content of nitrogen in dark areas (points 1, 3, 5 in Figure 3) and reduced content of nitrogen in light areas (points 2, 4 in Figure 3), which correspond to intermetallic layers. With the transition from the upper to the lower layers of the coating, an iron fracture increases, which could move from the investigated steel. The increased nitrogen content in point 6 as compared to points 2 and 4 is due to the nitrided layer that enters the scanning region.
There are no literature data on the effect of ion modification followed by deposition of ion-plasma coatings on the corrosion properties of UFG martensitic steels. The present study investigated the corrosion behavior of UFG martensitic steels subjected to ion-plasma treatment: ion nitriding followed by deposition of the TiAl$_3$/TiAlN coating.

**Table 1.** Atomic ratio of chemical elements in different points of TiAl$_3$/TiAlN coating

| Points | Atomic ratio, % |
|--------|-----------------|
|        | N   | Al  | Ti  | Fe  |
| 1      | 35.12 | 22.8 | 40.7 | 0.4 |
| 2      | 27.27 | 26.7 | 45.4 | 0.4 |
| 3      | 39.77 | 22.2 | 36.6 | 0.5 |
| 4      | 27.4  | 22.1 | 48.5 | 0.8 |
| 5      | 34.34 | 21.5 | 42.9 | 0.7 |
| 6      | 33.15 | 21.5 | 43.1 | 0.9 |
A comparison of corrosion rates for steel EI961 without subsequent coating in a 3% NaCl electrolyte showed that the corrosion rate for the CG structure is 2.5 times lower than that for the UFG structure. High activity of UFG steel is due to a significant decrease in grain size, elongated boundaries and high density of dislocations at the grain boundaries, which together lead to accelerated dissolution in interaction with the activating external environment. Steel corrosion mainly associates with oxygen depolarization. The resulting primary products Fe$^{+2}$ and OH$^-$ react to form white ferric hydroxide (II), which is oxidized by atmospheric oxygen to form brown ferric hydroxide (III):

$$4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3.$$  

Further transformation produces rust, i.e. complex hydrated ferric oxides:

$$n\text{Fe}_2\text{O}_3 + m\text{FeO} = q\text{H}_2\text{O}.$$  

Corrosion rate is controlled by the rate of oxygen diffusion to its surface in a sodium chloride solution.

Comparison of the corrosion rates for CG and UFG steel coated with TiAl$_3$/TiAlN showed a significant reduction in the corrosion rate (2 times for UFG steel and 4.7 times for CG steel). Significant corrosion effect with the deceleration of the corrosion rate by 2-5 times has been achieved. Increased corrosion resistance of UFG samples coated with TiAl$_3$/TiAlN is probably related to the presence of the first layer of nanocrystalline iron in the multilayer coating followed by a layer of titanium aluminum nitride with ultrafine grains and high lattice curvature. This unusual microstructure of the coating allows high-corrosion properties as compared to CG substrates.

The studies revealed that the samples subjected to ion nitriding + TiAl$_3$/TiAlN coating are more resistant to corrosion than the samples subjected to TiAl$_3$/TiAlN coating only. Comparison of corrosion rates for pre-nitrided UFG samples is 3 times higher than the corresponding value for the samples that were not subjected to nitriding prior to coating and 14 times higher compared to uncoated samples. Obviously, corrosion resistance of the samples subjected to ion nitriding and subsequent deposition of coatings is higher than that of the samples that were not nitried, in particular due to the gradient (as opposed to abrupt and step-like) transition of the substrate core (product) parameters to
the characteristics of the coating. Increased corrosion resistance was confirmed by continuity of the coating (Fig. 4) after the corrosion tests as compared to the other samples.

Figure 4(c) shows that the sample surface is characterized with shallow pitting of 0.01 mm depth. Pitting or corrosion holes in martensitic steels often have microscopic dimensions, are surrounded by reddish-brown or multi-colored corrosion products, often have circular deposits of corrosion products around the holes. In martensitic steel pitting corrosion is caused by chloride ions that penetrate through the passive steel layer in some areas.

Analysis of the surface microstructure of the coated specimens (Fig. 4 (d)) showed no corrosion; instead, the coating changed its color to dark gray. Thus, the surface of UFG samples experiences less significant corrosion attacks.

4. Conclusion
Corrosion tests of martensitic steels with coarse-grain and ultrafine-grain structure revealed that:

- Corrosion resistance of CG martensitic steels is 1.5 times higher as compared to the UFG samples. Therefore, the impact of the structure on the corrosion resistance should be taken into account when using UFG martensitic steels.
- Deposition of protective coatings TiAl3/TiAlN onto martensitic steels may increase the corrosion resistance of the CG materials by 8 times and of the UFG materials by 20 times.
- Ion nitriding prior to deposition of protective coatings can improve corrosion resistance only for UFG materials (22 times).

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