Electrochemical stability of nitride coatings for a steel – carbon fiber tribopair under conditions of imitation of a marine environment

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Abstract. The paper presents the results of comparative studies of TiCrNiN and TiCrMoNiN coatings deposited on X20Cr13 steel used in the manufacture of bearings for friction units of ship mechanisms operating in a friction pair with carbon fiber reinforced plastic. Using of the investigated coatings significantly improves the resistance of the product to corrosion in seawater.

Chromium stainless steels paired with carbon fiber reinforced plastic are used as bearing elements for friction units of marine machinery. At the same time, there is a problem of significant wear of the metal component of the friction pair, associated both with the tribological effect (wear during friction) and due to the effect of the corrosive environment of sea water. One of the ways to extend the service life of such units is the use of protective hardening coatings on the surface of steel products. Nitride coatings obtained by PVD methods are widely used to improve the physical and mechanical properties, as well as corrosion and wear resistance of tool materials and friction pairs.

In this case of bearing elements for friction units of marine machinery, we propose using TiCrNiN and TiCrMoNiN systems as possible protective coating compositions. A solid base made of TiN with the addition of nickel is designed to provide the coating with high hardness and increased wear resistance [1] due to transition from columnar structure inherent in pure TiN coatings to nanocrystalline structure; chromium inclusion should enhance the corrosion resistance and adhesion strength to the substrate in case of formation of CrN nitride phase in the coating material [2, 3]; the presence of molybdenum-containing phases should improve the tribological characteristics of the coating and its wear resistance under various types of impact [4, 5]. In addition, a positive effect of molybdenum on the electrochemical stability of TiAlN coatings in NaCl solutions has been reported in [6]. This paper discusses the issue of the stability of these compositions to the effects of an aggressive marine environment in order to determine the prospects of their practical application as protective wear-resistant coatings under these conditions.

The investigated coatings were deposited by the arc-PVD method on a X20Cr13 steel substrate using a two- and three-cathode evaporation system for the implemented systems. In the case of the
TiCrNiN system consumable cathodes of Cr (evaporating arc current \( I = 120 \, \text{A} \)) and Ti-50 at.% Ni (\( I = 125 \, \text{A} \)) were used. During the deposition of the TiCrMoNiN system Mo, Ti-Ni, and Cr cathodes were used with the values of the evaporating arc current of 125, 100 and 125 A, respectively. The bias potential applied to the substrate was 120 V. The deposition was carried out in Ar-N\(_2\) mixture at a nitrogen reactive gas partial pressure of 0.4 Pa. During deposition, the substrate was heated to 450°C. The deposition time was 90 minutes, the thickness of the resulting coatings was about 4 μm.

Electrochemical tests of coated and uncoated X20Cr13 steel samples were carried out at room temperature in a 3% aqueous solution of NaCl, simulating the environment of seawater [7], using an IPC-Pro potentiostat using a KCl reference electrode in a saturated KCl solution and a platinum auxiliary electrode. The potential sweep rate was 0.2 mV/s. Anodic polarization curves were recorded after reaching stationary potentials of the samples. After the tests, the surface of the studied samples was examined using Vega Tescan 3 SEM for the detection of pitting, the elemental composition of the surface layer was investigated by the EDX method.

The potentiodynamic curves (figure 1) recorded during the electrochemical tests show that the anodic curves of the three tested samples are characterized by the appearance of an activation peak in the region of the transition from the active to the passive state, which indicates the absence of the tendency of materials to self-passivation in marine environment. The activation peak for uncoated X20Cr13 is -302 mV, for TiCrNiN is -370 mV, for TiCrMoNiN is -215 mV.

**Figure 1.** Potentiodynamic curves recorded in a 3% aqueous solution of NaCl for investigated samples.

The potentiodynamic curve for steel represents a significant increase in the density of the anode current, which may be associated with the phenomenon of re-passivation or local dissolution of any of the elements that make up the alloy. However, in case of using TiCrNiN and TiCrMoNiN coatings we do not observe such density of the anode current growth which indicated lower corrosion speed in the used environment.

At the same time, the corrosion resistance of the TiCrMoNiN system is not significantly higher than that of the TiCrNiN system. From the polarization curve of the TiCrMoNiN coating, it can be seen that the presence of Mo leads to a potential shift in the positive direction, at a current density greater than \(-1.5 \, \text{mA/cm}^2\), which can indirectly confirm the high corrosion resistance of the system. Fluctuations of the passive state current in the regions of higher polarization potentials may indicate that the TiCrMoNiN system has a self-healing region from \(\approx -200\) to \(400 \, \text{mV}\).

Figure 2 shows SEM images of the surface of the investigated samples before and after electrochemical tests. The significant damage on the uncoated sample surface (figure 2b) indicates that...
X20Cr13 steel is significantly susceptible to corrosion and it does not show any resistance in an environment simulating seawater. As for the TiCrNiN and TiCrMoNiN coating systems before and after conducted electrochemical tests in a 3% NaCl solution (figure 2 c, d, e, f), there is no pitting or signs of other significant morphology changes on their surface, in contrast to uncoated steel.

Figure 2. Morphology of X20Cr13 steel, without coating (a, b), with TiCrNiN coating (c, d), with TiCrMoNiN coating (e, f) before (a, c, e) and after (b, d, f) electrochemical tests in 3 % NaCl solution.

The results of studying the elemental composition of coating samples using EDX method before and after electrochemical tests in a 3% NaCl solution are presented in table 1. The percentage of chromium, titanium, nitrogen before and after electrochemical tests change insignificantly for both systems, while the content of molybdenum after electrochemical testing is reduced by 2 times. This may be due to the tendency of molybdenum to form alkali metal molybdates when exposed to an alkaline environment, which is a used NaCl solution. At the same time, no Ni was found in the composition of the TiCrMoNiN coating after electrochemical tests, which may be associated with a decrease in its concentration in the coating below 1 at.%, which in this case is the sensitivity threshold of the composition analysis method. However, such changes in the elemental composition are not accompanied by noticeable phenomena of selective dissolution of the coating material with violation
of its integrity and loss of its protective function, which is confirmed by data obtained from potentiodynamic curves and SEM studies of the morphology of surfaces subjected to electrochemical tests. In general, the results indicate the stability of the composition and structure of the TiCrNiN and TiCrMoNiN coatings material under the implemented test conditions and the absence of signs of corrosion failure under the influence of an aggressive marine environment.

| Coating         | Composition before electrochemical test, at.% | Composition after electrochemical test, at.% |
|-----------------|-----------------------------------------------|---------------------------------------------|
| Ti-Cr-Mo-Ni-N   | Ti 15  Cr 26  Mo 10  Ni 2  N 47               | Ti 12  Cr 30  Mo 5  Ni 47                  |
| Ti-Cr-Ni-N      | Ti 14  Cr 29  Ni 7  N 50                      | Ti 9  Cr 36  Ni 4  N 51                  |

The obtained results indicate the potential high efficiency of the application of TiCrNiN and TiCrMoNiN coatings for protection of the X20Cr13 steel parts from the effects of an aggressive marine environment under conditions of operation on friction units of ship machinery. Nevertheless, the question of the wear resistance of the coatings under study in real operating conditions remains open and requires further studies of their stability under friction conditions, including in the presence of the influence of the seawater environment.

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