Tribological And Corrosion Characteristics Of Coatings Based On Chromium Nitride Deposited By The Mechanochemical Method

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Abstract. A study was conducted to evaluate the performances against wear and corrosion of Cr₂N thin films. The thin film was synthesized onto steel substrates SHKH15, using mechanochemical method. The experimental work was achieved using ball-on-disc configuration in dry conditions against Al₂O₃ balls. The corrosion resistance was determined by potentiometric method. The main conclusions are: corrosion testing in 4 % solution of nitric acid (HNO₃) solution indicated that Cr₂N is improved anticorrosion performance when compared to the steel substrate SHKH15; the Cr₂N coating presents the better tribological properties. Tribological tests against, that Cr₂N coating presents the lowest coefficient of friction relatively to the steel substrate SHKH15.

1. Introduction

Currently, there is a need to improve the protection of friction units against deterioration with the development of modern technology and traditional lubricant materials are not effective. For example, under poor or boundary lubrication conditions, the operating mode of rolling bearings is less favorable. In such cases, the formation of an oil film may not be possible, which results in direct contact of the metal surfaces of the rolling elements and rings and, thus, leads to wear when seized, such as corrosion-mechanical wear, and to premature failure. Due to these phenomena, the service life is greatly reduced under poor lubrication conditions. To mitigate this problem, attempts have been made to use hard coatings on bearing parts, for example, coatings containing carbide or nitride (for example, TiN, TiC, CrN), as well as solid lubricants, such as molybdenum disulfide. Although nitride and carbide coatings have high hardness and provide good abrasion resistance and high hardness, their friction coefficients are high. These high friction coefficients, combined with high hardness, lead to abrasive wear of the mating surfaces, i.e. surfaces of a ring or rolling body. In order to reduce the coefficient and improve the physical-mechanical characteristics of the coatings of binary systems (TiN, ZrN, AlN, etc.), additional alloying elements (Si, Cu, Al, Cr, etc.) are added to their composition [1]. Chromium-based coatings have gained importance due to their chemical inertness, thermal stability, and improved corrosion resistance compared to TiN coatings [2,3].

At the present time, mechanical-chemical synthesis is considered the most promising method of applying protective composite coatings to products from structural steels. This is evidenced by the large surge in the last decade of publications devoted to the study of the mechanism and kinetics of the growth of coatings on the surfaces of metals and alloys under various technological conditions of the
mechanical-chemical process. The mechanical-chemical method allows the formation of composite wear- and corrosion-resistant, dielectric and heat-resistant ceramic-like, as well as decorative coatings [4]. In this work, we studied the tribological and corrosion properties of Cr$_3$N coatings on the surface of SHKH15 steel (bearing structural steel) synthesized by the mechanical-chemical method.

2. Material and Experimental Procedure

SHKH15 steel was chosen as a research material which is widely used in the bearing industry (bearing rings, pressure valves, atomizer housings, pusher rollers). The chemical composition of steel SHKH15: C; 0.95-1.05 % Si; 0.17-0.37 % Mn; 0.2-0.4 % Ni; <0.3 % S; <0.02 % P; 0.027 % Cr; 1.3-1.65 % Ti; <0.01 % Cu; <0.25 % O; <0.0015 %. A thin coating based on chromium nitride was obtained on the surface of a 2 mm thick disk from SHKH15 steel on a vibration stand SVU2 [5] by the method of mechanical-chemical synthesis. The parameters for coating were selected: the amplitude of the vibration of 3.5 mm; oscillation frequency of 50 Hz; ball diameter 6 mm; the ratio of the mass of the powder to the mass of the balls is $m_p:m_m = 1:30$, the processing time by mechanical-chemical synthesis is 1 hour. The degree of filling of the chamber is 80-85 %. It was selected taking into account that the distance between the surface of the spherical layer and the material being processed was close to the magnitude oscillations (two amplitudes) to obtain maximum impact force of the balls.

The tribological characteristics of the coatings were studied by using a friction machine according to the ball-disk scheme. The experiments were carried out at room temperature 25 °C, a mean free path of 300 m and a load of 5N.

The corrosion of steel SHKH15 was determined by potentiometric method before and after applying a thin film coating of Cr$_3$N by mechanical-chemical alloying. A certain sample preparation was carried out to study the samples for corrosion resistance: copper wires with a cross section of 4 mm were soldered to each sample with the initial insulation, then the sample was varnished in several layers with drying for each layer, while leaving an uncoated sample area (20 % of the total area ) for research. The test procedure, potentiometric, is based on the dependence of the concentration / activity of ions in a solution with an electrode on the equilibrium electrode potential, i.e. EMF of a reversible galvanic cell consisting of electrodes immersed in the test solution, where the potential depended on the concentration of the determined ions, was measured. Corrosion tests were carried out on a potentiostat-galvanostat P150, in a 4 % solution of nitric acid (HNO$_3$). The phase composition of the samples was studied by X-ray diffraction analysis on an X’PertPro diffractometer by using CuK$_{\alpha}$-radiation.

3. Results and Discussion

The thickness of the Cr$_3$N coatings on the surface of SHKH15 steel is about 23 μm. The thickness of the coatings was evaluated by the calotest method. The technique consists in grinding the coated sample with a ball, the thickness of the coating is measured in accordance with the geometry of the track from the ball on the sample and the grinding ball. Optical analysis of the projection onto the plane of the resulting sphere-shaped recess on the coating and the matrix allows you to determine the thickness of the coating. Figure 1 shows the diffraction pattern of Cr$_3$N coatings on the surface of SHKH15 steel. A diffraction pattern broadens the diffraction lines of Fe and the formation of a diffuse background. Various changes in the diffraction lines of the sample after mechanochemical synthesis indicate the presence of defective structural states. A strong deformation effect on a substance, especially at low temperatures, is accompanied by the transfer of high energy to it and the formation of special, locally inhomogeneous states caused by saturation with defects and high stresses on small submicro- and nanoscale structural elements.
Figure 1. Diffraction pattern of steel SHKH15 with Cr$_2$N coating.

An analysis of the cross sections of the wear paths after testing indicates that there is virtually no wear after coating (Picture 2b). The coated sample has a coefficient of friction of 0.14-0.17. Note that in order to consider a particular material promising for its use in dry friction pairs, the material must have a low coefficient of friction (<0.2).

Figure 2. Fragments of the wear path and friction coefficient before (a, b) and after applying Cr$_2$N coatings (c, d) on the surface of SHKH15 steel.

Various methods are being developed to increase the service life of bearings in situations where lubricating oil pollution with salt water may occur with the aim of increasing the service life and reliability of bearings of gas turbine engines by increasing their corrosion resistance. If water or aggressive media penetrates into the bearing in such a volume that the lubricants cannot protect steel surfaces, corrosion will occur. In [6], the effect of heating on the corrosion properties of steels coated with TiN and CrN was investigated. The results of the study showed that samples coated with CrN coating showed better anti-corrosion properties than steel coated with TiN. The corrosion of steel SHKH15 was determined by potentiometric method before and after applying a thin film coating of
Cr$_2$N by mechanical-chemical alloying. Assessment of the corrosion behavior of the samples was carried out by the value of their electrode potentials, by measuring and regulating currents and voltages at the working electrode in the process of electrochemical studies. The test results showed that the corrosion rate of SHKH15 without coatings was 0.445 cm/year; after applying the Cr$_2$N coating, the corrosion rate was 0.191 cm/year, i.e. two times less compared to uncoated steel SHKH15. This behavior can be explained by the presence of chromium nitride in the coating, which plays a key role in the protection of steels, since the inclusion of highly stable chromium nitride can significantly reduce the corrosion rate through a passive film formed on the surface of the material [7]. In addition, chromium nitride has a high degree of chemical stability and good corrosion resistance [8].

4. Conclusions
It is possible to obtain a coating of chromium nitride by the method of mechanical-chemical synthesis on the surface of SHKH15 steel. The improvement of tribological and corrosion characteristics of SHKH15 steel after applying thin-film coatings based on Cr$_2$N deposited by the mechanochemical method is revealed. The experiment results showed that after the Cr$_2$N coating was applied, the corrosion rate was halved compared to uncoated SHKH15 steel. Decreasing in the friction coefficient by 2.5 times is observed after applying Cr$_2$N coatings. The decrease in the friction coefficient is explained by an increase in the wear resistance of the sample surface.

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