Effect of annealing on the morphology and mechanical properties of phosphorus-doped nickel coatings obtained by cathodic arc evaporation

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Abstract. The results of an atomic force microscopy study of the surface of nickel coating doped with phosphorus of 2 μm thick obtained by cathodic arc evaporation after the annealing at temperatures from 100 to 500 °C are presented. The surface morphology changes significantly with an increase in the annealing temperature. A negative high correlation between the specific surface energy and the coating roughness after the annealing was established. The mechanical properties (microhardness, elastic modulus and plastic deformation) were determined by nanoindentation. A decrease in the elastic modulus of the nickel coating with an increase in the annealing temperature was found.

1. Introduction

Nickel coatings are widely used for the corrosion protection of various parts made of steel and other alloys. Such coatings are often used to increase the wear resistance of rubbing surfaces [1, 2]. These coatings have high hardness and wear resistance, and they are also resistant to the aggressive media [3]. Additives of small amounts of non-metals are widely accepted to modify the crystal lattice of the coating and thus its properties [4]. To improve their physical and mechanical properties, phosphorus is added to the nickel coatings [5]. Doping the coating with phosphorus (1–2 at.%) leads to an increase in the microhardness by several GPa [1]. Phosphorus-doped nickel coatings exhibit significantly better corrosion resistance than pure nickel [3].

Cathodic arc evaporation of nickel is an environmentally friendly technology compared to the electrochemical deposition or vapor-phase metallization in vacuum. Chloride-sulfate, acetate-chloride, nickel sulfate, magnesium sulfate and other electrolytes are used in the electrolytic deposition [1, 3]. Such electrolytes require proper processing and disposal. In the vapor-phase metallization process, while obtaining the ultrapure nickel coatings, poisonous carbonyl vapors are released, requiring an additional complex ventilation system to completely eliminate the vapors contact with humans.

Annealing of nickel coatings leads to an altering in the surface structure and phase composition [6], as well as their physical and mechanical properties. Due to the high melting point of nickel, nickel-based coatings can be applicable as wear-resistant protective coatings on tools operating at high temperatures up to 600 °C [7]. Annealing at temperatures of 100–500 °C allows simulating the...
temperature effect on the coating during the tribological contact [8]. Under the annealing influence at temperatures of 400–500 °C, an oxide film appears on the coating surface, as well as a new oxide phase NiO, which leads to an improvement in the wear-resistant properties of the coating at high temperatures [9]. The phosphorus-doped nickel coatings exhibit the better wear-resistant properties at temperatures above 400 °C due to the structural changes and the formation of the nickel phosphide phase Ni₃P [9].

The aim of this work is to investigate the effect of annealing on the structure, surface roughness and mechanical properties of the nickel coating doped with phosphorus obtained by the cathodic arc evaporation.

2. Experimental details
The nickel coatings were applied by the cathodic arc evaporation in the “Bulat” device. The evaporated cathode contained 6% of phosphorus, the cathode arc current was 100 A, and the substrate voltage bias was -50 V. The coating of 2 μm thickness with phosphorus concentration of 2 at. % was applied to the 321 stainless steel substrate.

The coating was annealed in SNOL 8.2/1100 oven (Lithuania) at room atmosphere and relative humidity of 40%. The annealing temperatures used were 100, 200, 300, 400 and 500 °C. The heat treatment mode was as follows: the sample was heated at a rate of 10 °C/min to the set annealing temperature, then held for 30 minutes at this temperature, then the sample was cooled together with the chamber to room temperature.

Investigations of the surface microstructure [10], quantitative determination of roughness and adhesion forces were carried out on Dimension FastScan atomic force microscope (AFM) (Bruker, USA) in the PeakForce QNM mode using a standard silicon cantilever of the CSG10_SS type (TipsNano, Russia) with tip radius of 5 nm and console stiffness of 0.21 N/m. The adhesion force was estimated by removing the AFM probe from the sample surface as the force required to break the “AFM probe-surface” contact [11]. The specific surface energy was determined by the ratio of the adhesion force $F_{ad}$ to $2\pi R$, where $R$ is the radius of the probe tip.

The microhardness $H$ and the elastic modulus $E$ measurements were carried out using Hysitron 750 Ubi nanoindenter (Bruker, United States) by introducing a spherical diamond indenter with a radius of 226 nm into the surface. 9 measurements with a constant load of 1 mN were carried out on each sample. The plastic deformation $\eta$ was determined from the indentation curves.

3. Results and discussion
AFM images ($3 \times 3$ μm²) of the coating surface in the initial state (at 20 °C) and after annealing are shown in figure 1. Comparison of the morphology and roughness of the coating surface was carried out in fields of several sizes. It was found that with an increase in the annealing temperature, the surface structure changes significantly. On the original surface (at 20 °C), a granular surface structure is visible and the grains form chains (figure 1 a). The surface morphology of the coating is very similar to the structure given in [5]. In this case, the grain size is 100–200 nm.

At an annealing temperature of 100–400 °C, the chains of grains become less noticeable, and smaller grains appear (figure 1 b-e). At 500 °C, the coating surface completely becomes fine-grained, the grain size varies from 40 to 70 nm.

When studying the surface morphology by AFM, the roughness ($R_a$, $R_q$, $R_z$) was determined (figure 2 a). The quantitative data of roughness are presented from a field of $3 \times 3$ μm². As can be seen from the graph (figure 2 a), the roughness decreases upon annealing from 100 to 300 °C. This is due to a decrease in the size of grains on the surface, filling of depressions with newly formed grains. At an annealing temperature of 300 to 500 °C, the grains begin to actively increase in size, leading to an increase in surface roughness. Also, an increase in roughness is associated with the formation of an oxide film on the surface [9].

As a result of the specific surface energy determining, it was established: the less the surface roughness, the higher the adhesion force on the surface, and hence the higher the specific surface
energy. In this case, the correlation is negative and amounts to $C_{corr} = -0.7–0.8$. This correlation is confirmed by the results obtained in [12–14]. They determined the value of the adhesion force depending on the surface roughness of titanium films, AlN coatings and multilayer metal-carbon coatings of various thicknesses.

![AFM images](image)

**Figure 1.** AFM images ($3 \times 3 \mu m^2$) of the nickel coating surface at different temperatures: a – 20 °C; b – 100 °C; c – 200 °C; d – 300 °C; e – 400 °C; f – 500 °C; g – surface profiles.

The values of the elastic modulus of the coating of the initial coating surface of 175 ± 19 GPa are close to the values of the elastic modulus of the pure electrolytic nickel coating in [15]. At an
annealing temperature of 100 °C, the elastic modulus increases to 195 ± 12 GPa. In this case, the microhardness decreases from 10.4 ± 0.8 GPa to 7.8 ± 0.4 GPa. With an increase in the annealing temperature from 100 to 500 °C, the modulus of elasticity of the coating decreases from 195 ± 12 GPa to 155 ± 24 GPa.

The microhardness in the temperature range from 100 to 400 °C remains practically constant, and at 500 °C it increases to 8.2 ± 1.4 GPa. Plastic deformation at temperatures of 100–400 °C remains practically unchanged. At 500 °C, it decreases to 88.1 ± 2.5%. This is due to an increase in microhardness at a given temperature. An increase in microhardness after 400 °C is associated with the formation of a new Ni3P phase [9].

![Figure 2.](image1.png)

**Figure 2.** Dependences of the coating roughness (a), adhesion force $F_{ad}$ and specific surface energy $\gamma$ (b) on the annealing temperature.

![Figure 3.](image2.png)

**Figure 3.**Indentation curves (a) and dependence of mechanical properties (b) on annealing temperature.

4. Conclusions

The surface morphology and the mechanical properties of the nickel coating doped with phosphorus were determined using atomic force microscopy and nanoindentation.

The annealing of nickel coating from 100 to 500 °C leads to the significant changes in the microstructure and roughness of the coating surface in comparison to the initial surface.

The high correlation of the specific surface energy with the roughness has been established.

It was found that the elastic modulus of the coating decreases with an increase in the annealing temperature. The microhardness remains practically unchanged till 400 °C and increases at 500 °C.
According to [7, 9], the significant changes in the surface morphology and an increase in the microhardness after 400 °C is associated with an increase in the crystallization degree of the coating, appearance of oxide film on the surface and formation of the new Ni$_3$P phase.

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