

Electroless Ni-P-Al₂O₃ composite coatings

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Abstract

The paper discusses experimental investigations aiming at the determination of appropriate conditions for the chemical deposition of Ni-P-Al₂O₃ composite coatings. The structure, microhardness, and abrasive wear of deposits on steel St3S (0.3 % C) were studied. An electron-scanning microscope was used to analyse the structure of the layers. The phase composition of the coatings was determined using a diffractometer. The profile of roughness was analysed with a profilographer. Adhesion was tested as well. The analyses of the properties of the Ni-P-Al₂O₃ deposits confirm that the presence of the dispersion phase of aluminium oxide affects the resistance of the coating to mechanical destruction.

Key words: outer layer, composite coatings, micro-dispersive grain, electroless deposition, wear resistance

1. Introduction

Ever since the first composite materials were developed, the goal has been to achieve a combination of properties not obtainable by any of the ingredients alone. The use of dissimilar materials can result in the production of composite solids with a wide range of mechanical, magnetic, chemical, electrical and optical properties. The properties, however, depend on the composition of the distributed and matrix phases. Metal matrix composites with ceramic particles acting as the distributed phase are being widely applied as anti-wear, anti-frictional engineering materials [1].

The industrial use of electroless nickel-phosphorus coatings, in both their basic form and as composites with ceramic dispersions, is well established. Composite coatings based on single metal electrodeposits have received particular attention. As far back as 1950, Brenner discussed the electrodeposition of nickel-phosphorus coatings. Although the process has had little application in industry, there are numerous works concerning the structure and properties of deposits obtained in this way [2].

The latest development in electroless Ni-P deposition is the co-deposition of solid particles within coatings. These solid particles can be hard materials (SiC, B₄C, Al₂O₃, diamond) or dry lubricants (PTFE,

MoS₂ and graphite). This method can be used to produce composite layers with very good characteristics for specific applications. Electroless Ni-P-SiC coatings are known to be hard and wear resistant, so they can replace “hard chromium” in the aerospace industry. Also, the electroless Ni-P-PTFE films show excellent self-lubricating properties [3].

Chemical, catalytic deposition of metals and alloys is a popular method of metal plating [4, 5]. The process is dependent on redox reactions. The method of chemical deposition of metal and ceramic coatings obtained from dispersive material suspensions in a plating bath has been known since the 1960s. At present, new technologies are being developed for various coatings.

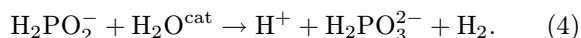
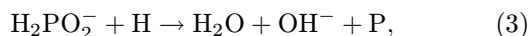
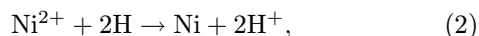
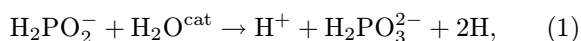
In the process of catalytic deposition of coatings, no external source of electric current is used, yet the plating is connected with the flow of electric loads – electrons – from a different metal with a more negative electric potential or from a reducing substance. The amount of metal deposited per time unit depends neither on the current intensity, nor on the distribution of the electric field. It is possible to produce coatings with uniform thickness on a whole workpiece, provided there is an access to all surfaces during the bath. Electroless nickel deposition represents an alternative method, if different – metallic and nonmetal-

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lic – substrates are used. The process is based on a redox reaction in which the reducing agent is oxidized and Ni^{2+} ions are reduced on the substrate surface. Once the first layer of nickel is deposited, it acts as a catalyst in the process. As a result, a linear relationship between the coating thickness and time usually occurs. If the reducing agent is sodium hypophosphite, the obtained deposit will be a nickel-phosphorus alloy. The co-deposited Ni-P alloys were reported to have a non-equilibrium phase structure. It is generally accepted that the microcrystalline, amorphous structure and the coexistence of these two phases depend on the phosphorus content [2, 3].

2. Experiment

By applying the two materials, i.e. a metal and a ceramic, which differ in properties, we obtain a two-phase material with a complex composite structure. Electroless deposited nickel-based coatings contain 7–15 % of phosphorus. They can be deposited directly on steel, iron, nickel, cobalt, aluminium and aluminium alloys. Metals that are not reduction catalysts, e.g. copper and brass, are coated by momentary contact with a catalytic metal. As soon as the first nickel nuclei are generated on the surface, the reaction proceeds spontaneously in the form of autocatalysis [4]. The process of Ni-P deposition is described by the following chemical reactions:



Applying an Ni-P- Al_2O_3 composite coating simultaneously with an Ni-P coating, we observe a dispersion of Al_2O_3 grains on the surface material. The process depends on: bath temperature, bath composition (Table 1), type of bath, pH, component concentration, mixing intensity, grain structure of the nonmetallic dispersion phase, matrix metal, and surface state [4, 5].

The method possesses numerous advantages. It permits producing composite coatings with a metal

Table 1. Bath composition

Components of bath	Amount (kg/m ³)
NiCl_2 (nickel (II) chloride)	50
NaH_2PO_2 (sodium hypophosphite)	20
CH_3COOH (glacial acetic acid)	8
CH_3COONa (sodium acetate)	12
Thiourea	0.015
Al_2O_3 (aluminium oxide)	4

matrix at a relatively low temperature of 358–368 K and pH ranging 4.1–5. The 4-hour process can be controlled easily. Additionally, it is possible to deposit top coatings with uniform thickness identical in the whole area. In the experiment, the coating was superimposed on a surface of carbon steel St3S. The allotropic variety of aluminium oxide – corundum – was used to produce Ni-P- Al_2O_3 composite coatings. The α - Al_2O_3 variety is characterized by high hardness 9 on the Mohs scale, high temperature of melting 2323 K, good thermal stability and high resistance to the action of chemical agents [6]. Table 2 shows the properties of the standard 99.5% aluminium oxide used in the process of deposition of Ni-P- Al_2O_3 coatings.

3. Results and discussion

3.1. Structure of composite coatings

The properties of the composite coatings depend not only on the selection of components but also on the structure of this composite – advanced material [7]. The structure of the Ni-P- Al_2O_3 coating is influenced by both geometry and dispersion of aluminium oxide as well as many other factors accompanying the process [7]. To analyse the structure of the composite coatings an electron scanning microscope and a light microscope were used. By means of the JEOL JSM 5400 electron scanning microscope equipped with an EDXS OXFORD INSTRUMENT ISIS 300 spectrometer, it was possible to analyse the chemical composition of the alloy coating with microdispersive particles. The surfaces of the composite coatings and their cross-sections were analysed by means of the above-mentioned microscope. The tech-

Table 2. Characteristics of aluminium oxide particles

Particle type	Shape	Density (kg/m ³)	Hardness, HV	Size (μm)
α - Al_2O_3	irregular	3970	2100	< 1

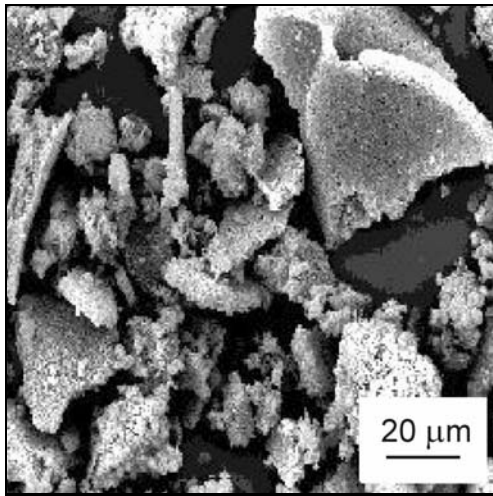


Fig. 1. An SEM view of the aluminium oxide powder.

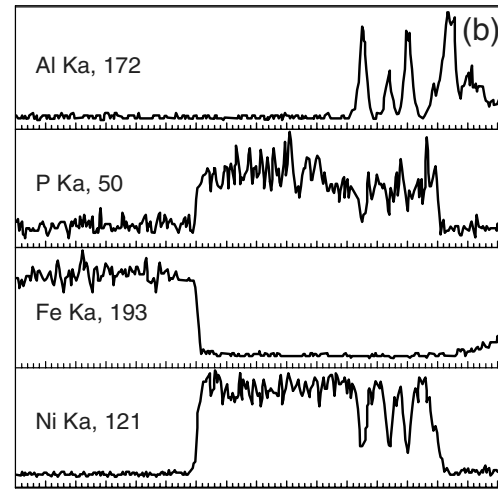
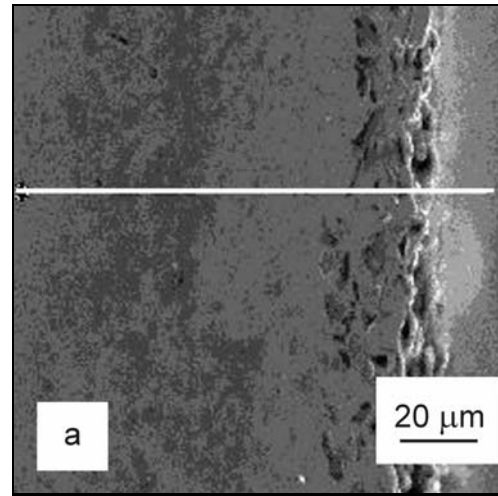
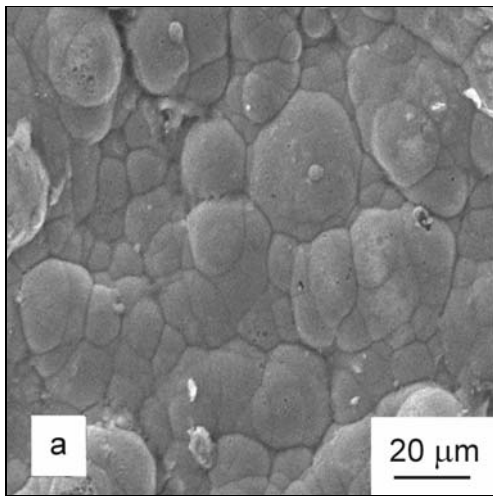


Fig. 3. Cross-sectional SEM view of the composite coating structure (a) and the linear distribution of the elements (b).

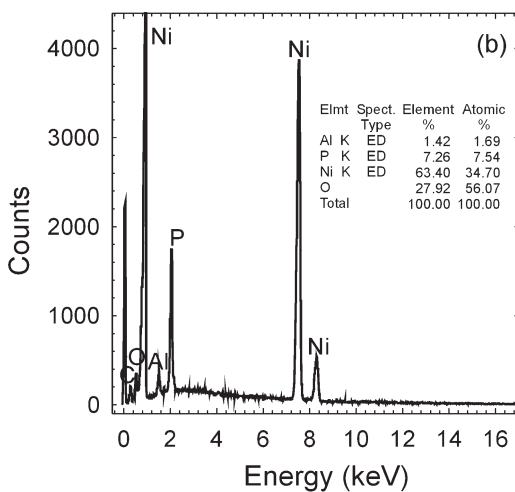


Fig. 2. An SEM view of the structure of the Ni-P-Al₂O₃ coating (a) and the EDXS method analysis (b).

niques employed in the investigation allowed us to observe the surface, the distribution of the dispersion phase grains in the layer volume, and to measure the thickness of the composite coatings. Figure 1 presents the aluminium oxide powder. A characteristic view of Ni-P-Al₂O₃ composite coatings and the chemical EDXS analysis are shown in Fig. 2. The cross-section of the layers and the linear distribution of the elements are illustrated in Fig. 3.

The SEM method was used to study the distribution of nickel and aluminium in the coating along selected scanning lines and in the area of a cross section. It was reported that the phase structure was the same as the desired one. From the analysis of the experimental data it follows that the content of the dispersion phase of the aluminium oxide in a plating bath affects both the surface topography and the coating structure. The microscopic observation of the composite coating showed that the ceramic powder particles

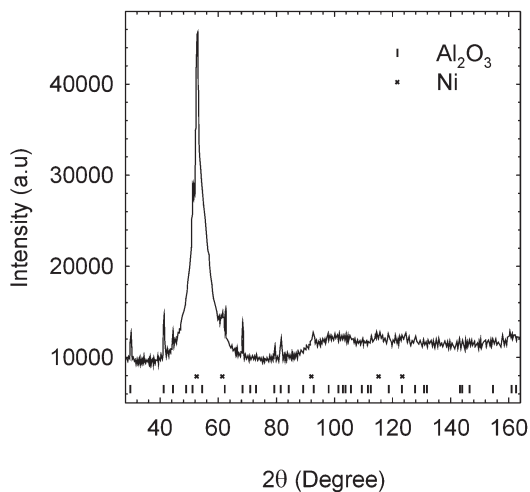


Fig. 4. The diffraction pattern of Ni-P-Al₂O₃ coating.

were surrounded by the nickel matrix. No discontinuity of the material was reported. The analysed coatings were characterized by quite a uniform distribution of particles of the dispersion phase of aluminium oxide in the nickel matrix and the same thickness of the coating. The investigation shows that the high quantity of alumina particles can be uniformly distributed in the nickel matrix using the proposed composite coating method.

The X-ray diffraction analysis of Ni-P-Al₂O₃ composite coatings was performed with a D8 Advance diffractometer made by Bruker using filtered radiation $\lambda\text{CoK}\alpha$ with a wavelength of 0.179 nm. The qualitative phase analysis was conducted applying the method of computer-aided matching of Ni and Al₂O₃ diffraction lines and the JCDD file. The influence of the diffraction pattern of Ni-P-Al₂O₃ coating is presented in Fig. 4.

The Ni diffraction lines are considerably broadened, and the whole X-ray diffraction view includes a powerful component of X-ray diffraction resulting from the amorphous phase. It means that the obtained Ni-P-Al₂O₃ coating is composed mainly of ordered regions of the near range.

3.2. Properties of Ni-P-Al₂O₃ coatings

The light microscopic examinations were combined with microhardness measurement. The Vickers test was conducted at a load of 200 g using a Zwick 3212 hardness tester. The results are presented in Table 3. In order to compare the influence of Al₂O₃ particles on the coating hardness, it was essential to measure the hardness of the composite coatings, of the nickel coatings and of the substrate material.

After deposition, the coatings were ground and polished. Their roughness was analysed with a Talysurf 4

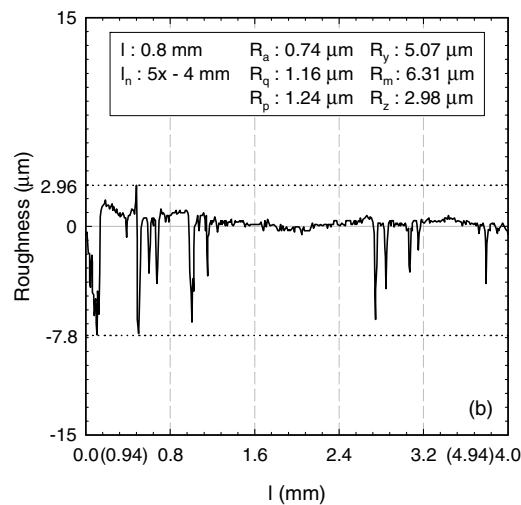
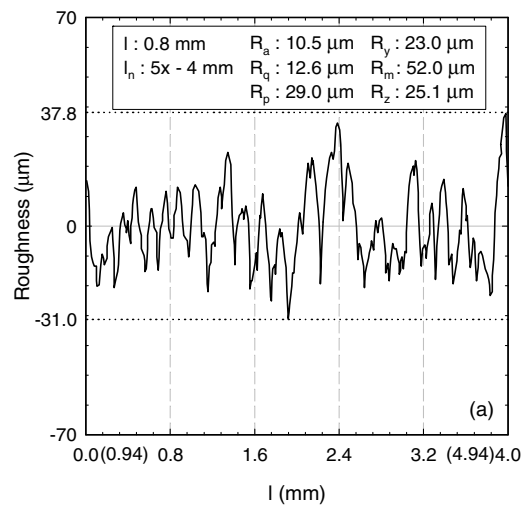


Fig. 5. Profiles of roughness: before (a) and after grinding (b).

Table 3. Results of the microhardness measurement

Material	St3S	Ni coating	Ni-P-Al ₂ O ₃ coating
Hardness 0.02 HV	168	196	608

profilographer at the Chair of Mechanical Engineering and Metrology of the Kielce University of Technology [8]. Figure 5 illustrates profiles of roughness and their parameters.

Tribological research carried out on T-01 machine running in pin-disk configuration enables assessment of friction and wear character in time at constant load, temperature and surroundings humidity value on the

Table 4. Material weight loss

Loss in weight (g)	
Sample 1	0.019
Sample 2	0.032
Sample 3	0.024

basis of friction force and wear quantity recording [9]. The testing with a T-01M device involved measuring the surface of rings after grinding and polishing [10]. Tribological curves were obtained during the research under technically dry friction conditions for friction junction of steel 55-surface layer on the layer of steel St3S at load $P = 9.81$ N and planning speed $v = 0.25$ m/s under the relative humidity conditions 62 ± 5 % and surroundings temperature $T_0 = 23 \pm 1$ °C. The chemical composition of steel 55 was characterized: 0.53–0.58 % C, 0.1–0.3 % Si, 0.3–0.6 % Mn, 0.035 % P, 0.035 % S, ≤ 0.2 % Cr, ≤ 0.08 % Mo, ≤ 0.2 % Ni, ≤ 0.2 % Cu. During the experiment the friction force was calculated and the material weight loss resulting from the friction pair operation was measured. The curves are presented in Fig. 6 and the Table 4 shows results of material weight loss.

The diagram shows that coefficient of friction increases stochastically in the initial part of tribological investigations, which is an effect of interaction between elements of friction junction model and close surroundings environment, since the transformation of technological surface layer proceeds and the layer changes into an exploitation layer, which presents other characteristics in the close contact area.

Composite material in the form of surface layers influences reduction of surface layer wear, but causes increase of coefficient of friction at technically dry friction. In exploitation technology for friction junction composed of elements with such layers reduction of friction resistance – coefficient of friction proceeds by applying appropriate lubricants [11].

Also, the adhesion of the Ni-P-Al₂O₃ coatings was tested for conformity with standard PN-EN 582 [12]. Five samples with a diameter $\varnothing 25.0$ mm made of steel St3S were prepared. After adhesion the samples were

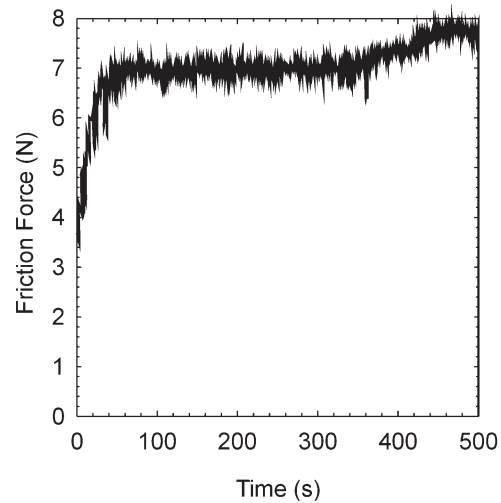


Fig. 6. The variation of friction force in time of friction junction: steel 55 – Ni-P-Al₂O₃/steel St3S at load $P = 9.81$ N, rotational speed $n = 600$ rpm.

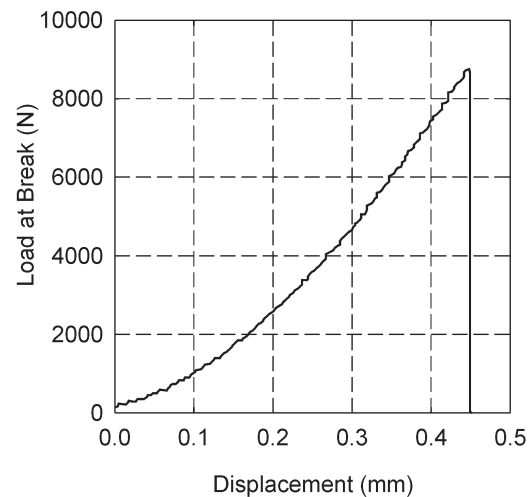


Fig. 7. Dependence of the load at break on displacement for Sample 5.

fixed in an articulation workholder. The adhesion was tested with the Instron 8501 resistance tester. The investigations were conducted at a shift velocity of 0.05

Table 5. The investigation results of adhesiveness

Sample	Load at break (kN)	Adhesion (MPa)	Average adhesion value (MPa)	Standard deviation
1	5.671	11.560		
2	4.539	9.249		
3	7.192	14.660	13.496	2.922
4	6.937	14.140		
5	8.771	17.870		

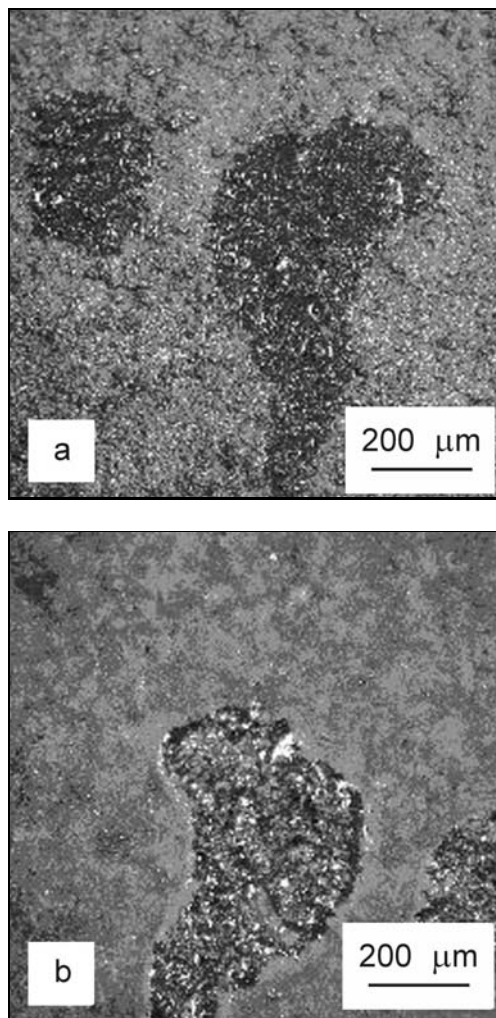


Fig. 8. The views of (a) the sample and (b) the antisample after the adhesion test.

mm/s. Adherence R_H was calculated as the average value of the five samples. The results of the investigations are given in Table 5 and the dependence of the load at break on displacement is illustrated by Fig. 7.

The results of the adhesion test for the Ni-P-Al₂O₃ composite layers after the adherence test are illustrated in Fig. 8. The photographs show that the composite coatings are not completely separated from the substrate, which is due to the partial separation of the Ni-P-Al₂O₃ coating from Ni-P coating.

4. Conclusions

1. It has been established that the deposited layers with Al₂O₃ micro-dispersive grains are characterized by process repeatability, so it is easy to control parameters such as time, pH and temperature.

2. The surfaces are characterized by evenly distributed volume dispersion of aluminium oxide particles and by identical thickness of the whole coating.

3. Few pores are observed in the coatings.

4. The positions of high-angular peaks of the Ni phase indicate the displacements related to the presence of a Ni-P solid solution and to the macroscopic internal stresses.

5. The microhardness of the Ni-P-Al₂O₃ coating is relatively high.

6. The results of the EDXS analysis verify the required distribution of elements in the produced layer.

7. The Ni-P-Al₂O₃ composite coatings are cohesive and can be machined by grinding.

8. The weight loss of Ni-P-Al₂O₃ composite layers after the wear test is decidedly lesser than that of Ni-P layers.

9. It has been reported that the adherence of the Ni-P-Al₂O₃ to the Ni-P coating was better than that of the Ni-P coating to the matrix.

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