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Characteristics and Properties of Chromium Coatings with Diamond Nanoparticles Deposited Directly on Aluminum Alloys

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Abstract

The objective of this study was to deposit directly chromium with diamond nanoparticles (ND) on aluminum alloys and investigate the coating surface. The chromium coatings on aluminum alloys were obtained by electrochemical deposition. The coatings were doped with ND. The diamond nanoparticles were obtained by detonation synthesis. Chromium coatings were deposited on aluminum alloys with a silicon content of 7 % and 10 %. The ND concentration in the electrolyte was 25 g/l. The surface analysis was performed by means of Atomic force microscopy. The surface of the coating of chromium with ND on Al10Si is twice more even than that on Al7Si. The microstructure and microhardness were examined with a metallographic microscope and a microhardness tester. The microhardness of the coated samples is 9163 MPa compared to 893 MPa of uncoated aluminum samples. The thickness of the chromium coatings doped with diamond nanoparticles is between 45 – 55 μm. The coatings are dense, continuous and uniform with good adhesion to the substrate material.

Keywords: Chromium coating, Aluminum alloy, Diamond nanoparticles, Atomic force microscopy, Wear resistance

1. Introduction

The main advantage of the aluminum alloys as structural elements and components is their light weight, ductility, corrosion resistance and relatively good strength and heat resistance. The poor microhardness and wear resistance are usually improved by applying coating on the surface. Chromium coatings on aluminum alloys increase their hardness to 65-70 HRc [1]. Chromium composite coatings with diamond nanoparticles further increase the listed above properties of the aluminum alloys. For example, chromium coating on aluminum possesses microhardness of about 6800 MPa, and the microhardness of chromium coating doped with ND go up to 11800 MPa [2].

The objective of the present research is to prepare composite chromium coatings with diamond nanoparticles directly (without intermediate layer) on aluminum alloy with different content of Si, 7 and 10 %, also called silumin. The structure and the morphology were studied and the microhardness and the wear resistance were determined also. The aluminum alloy (the substrate) contains 6.5 – 7.5 wt % silicon and respectively 9.5 – 10.5 wt % for the more rich in silicon alloy. The other components are Mn – 1.5 wt %, Fe - 0.19 wt %, Mg - 0.6 wt %, Cu - up to 0.5 wt % and aluminum the balance.

In order to apply a coating on any metal its oxide layer must be properly removed immediately before the coating is applied. In our case the oxide layer of aluminum (Al_2O_3) must be removed. It is a difficult process to reduce the oxide to metallic aluminum and the reverse reaction appears very quickly after the cleaned surface is exposed to air. The aluminum substrates are usually chemically treated (etched) in nitric acid, hydrochloric acid and acid-alkaline solutions. Another type of pretreatment to remove the oxide layer is electrochemical polishing in the respective electrolyte composition. This process is used to achieve accurate dimensions of the component before applying protective coatings. The removal of certain amount of metal from the surface is determined by the concentration of the chemicals, the temperature of the solution and the flow on the surface. By controlling these parameters the repeatability of the process can be controlled.

2. Experimental

The objective of this study was to deposit chromium directly without intermediate layers doped with diamond nanoparticles on aluminum alloys containing silicon. Industry uses several separate processes for optimal adhesion of chromium to the aluminum surface [3, 4]. First the aluminum casting is electroplated with a heavy deposit of copper. The copper layer is activated and finally chromium is electroplated. Another approach is to apply zinc immersion film called a zincate prior to the chromium electroplating.

The characteristics and properties of the modified with ND chromium coating electrodeposited on aluminum alloys were studied. These were microstructure, morphology, microhardness and wear resistance. The microstructure was studied with a Polyx Met metallographic microscope at 200× magnification, ProgRes CT3 USB digital camera and a licensed ProgRes CapturePro software product. The microhardness was measured using a PolyvarMet 4000 microhardness tester. The surface topography was studied by means of Atomic force microscope. AFM imaging was performed on the NanoScope V system of Bruker Inc.

The test samples were cylinders with diameter 15 mm and height 30 mm. The samples were first grinded, then degreased and finally treated with a special acid-alcaline solution before being suspended on the cathode and immersed in the chromium plating electrolyte. A standard chromium plating electrolyte has been used in the present study [5]. It has the following chemical composition:

CrO_3 – 220 g/l;
H_2SO_4 – 2.2 g/l

The electrochemical parameters of the process were:

Current density – 45 A/dm^2
Duration – 50 min
Temperature of the electrolyte: 50 – 55 ^oC
Anodic electrode – Pb alloy

The diamond nanoparticles were obtained by detonation synthesis and they were in the form of an aqueous suspension. The ND were pre-activated by ultrasonic treatment and added to the standard chromium electrolyte at a concentration of 25 g/l. The cylindrical aluminum specimens were suspended on the cathode, where electrodeposition of chromium metal took place.

3. Research, results and discussion

3.1. Structure and microhardness

The microstructure of the chromium coating deposited on aluminum alloys in electrolyte with 25 g/l ND was observed. Figure 1 presents the chromium coating on aluminum alloy with 7 % silicon (CrND/Al7Si) and Figure 3 – with 10 % silicon (CrND/Al10Si). It is clearly seen from the microstructure presented in Figure 1 that the chromium layer is continuous, with a thickness of about 45 µm. The layer is relatively uniform, following the surface of the aluminum matrix. The microhardness of the layer, shown in Figure 2, was determined and the measured microhardness is 9163 MPa and it is approximately 10 times greater than the microhardness of the matrix - 893 MPa.

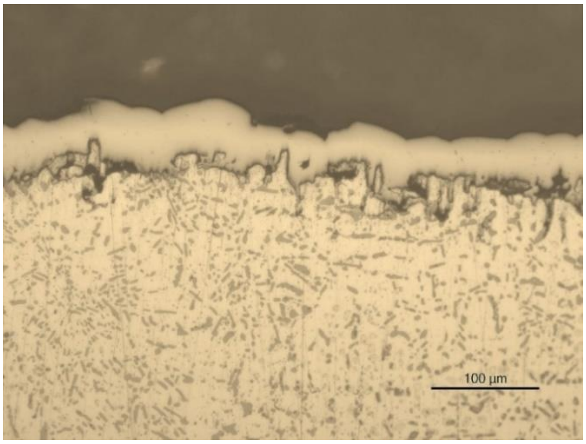

Fig. 1. Microstructure of chromium coating with ND deposited on aluminum alloy containing Si 7 %

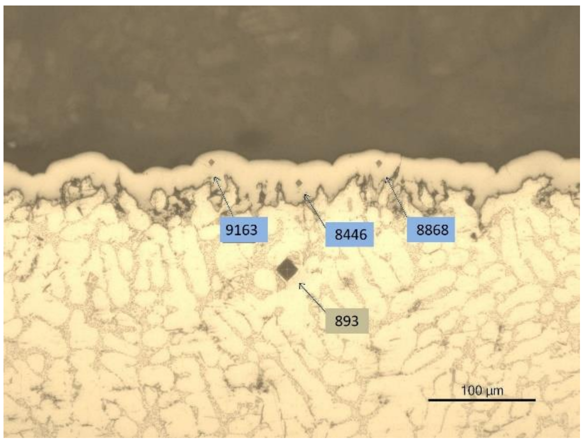

Fig. 2. Microhardness of chromium coating with ND deposited on aluminum alloy containing Si 7 %

It is clear from the microstructure presented in Figure 3 that the chromium layer is continuous, with a thickness of about 50 µm. It is uniform, following the surface of the aluminum matrix containing 10 % silicon. The microhardness of the layer (Figure 4) was about 8290 MPa and approximately 8.5 times greater than the microhardness of the matrix - 972 MPa.

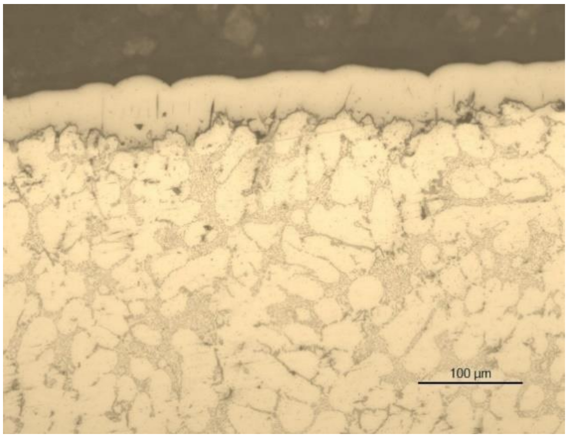

Fig. 3. Microstructure of chromium coating with ND deposited on aluminum alloy containing Si 10 %

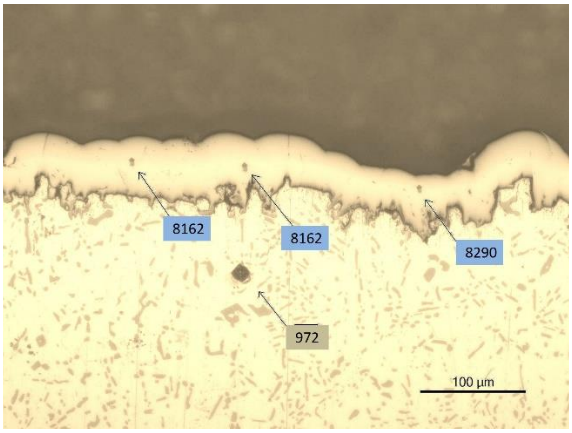

Fig. 4. Microhardness of chromium coating with ND deposited on aluminum alloy containing Si 10 %

The following summary can be made from the performed comparative analysis. The chromium coating with ND deposited on an aluminum alloy with 7 % Si is less thick with about 4 µm and it is more uneven than the coating on an aluminum alloy with 10 % Si. On the other hand, the microhardness of the coating on the aluminum alloy with 7 % Si is approximately 9 % harder than the coating on the aluminum alloy with 10 % Si. There is no logic explanation for this phenomenon except for the different silicon content. Regarding the microhardness of the matrix the Al alloy with increased Si is harder. As a rule, with increasing the silicon content in aluminum alloys, their castability and hardness also increase.

3.2. Surface morphology

The surface topography was studied by means of Atomic force microscopy. AFM imaging was performed on the NanoScope V system (Bruker Inc., Germany) operating in contact mode in air at room temperature. Silicon cantilevers (ContE-G, Budget Sensors, Innovative solutions Ltd, Bulgaria) with 30 nm thick aluminum reflex coating were used. The scanning rate was set at 2 Hz and the images were taken in the highest possible resolution mode of the AFM, 512 x 512 pixels in JPEG format using the NanoScope software.

Traditionally, AFM has been used to measure the surface topography by direct contact between the surface and the tip of the sonde mounted at the end of the cantilever. AFM images were obtained by scanning a sonde on the sample surface using piezoelectric scanners. AFM's high-resolution imaging capability allows for accurate location of concavity locations and measurement of their depth [6].

The morphology of the surface of the chromium coating with ND deposited on an aluminum alloy with different percentage of Si was studied and characterized. Atomic force microscopy (AFM) was applied and the obtained images are presented in Figures 5, 6 and 7. Figure 5 is a typical image of the AFM height in 2D format of Cr ND coating deposited on Al7Si with a different scan area of 1.5 × 1.5 µm^2 (Figure 5A) and a scan area of 5 × 5 µm^2 (Figure 5B), respectively. These images are accompanied by cross-section of the chromium coating surface.

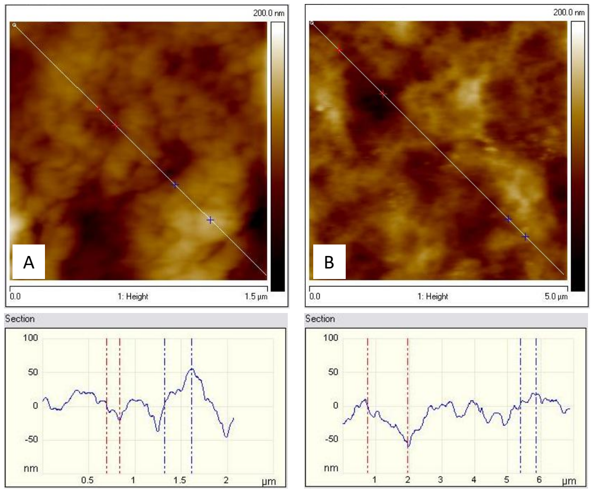

Fig. 5. 2D topography of chromium coating with ND on aluminum alloy containing 7 % Si

Figure 5A presents the roughness profile in 2D AFM image, where the scanned area is 1.5 × 1.5 µm^2 and z-range = 200 nm with image cross section.

Figure 5B presents the roughness profile in 2D image, where the scanned area is 5 × 5 µm^2 and z-range = 200 nm with the image cross section.

The diagonal sectional analysis of the scaned zone in the z-band z = 200 nm showed that the surface of the chromium coating deposited on an aluminum alloy with 7 % silicon is relatively smooth.

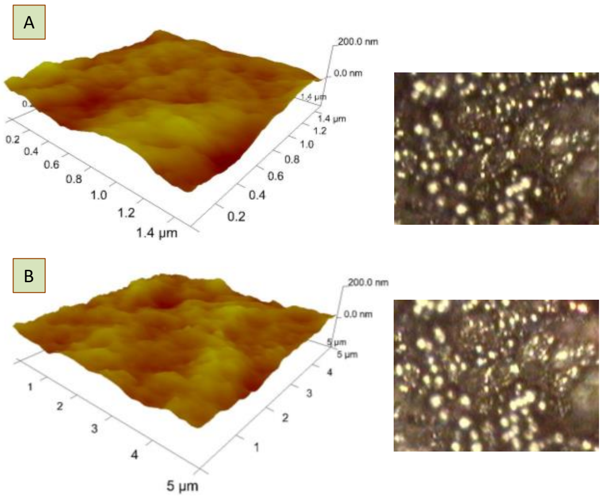

Fig. 6. 3D topography of chromium coating with ND on aluminum alloy containing 7 % Si

Figure 6A presents the roughness profile in 3D AFM high resolution image, where the scanned area is 1.5 × 1.5 µm^2 and z-range = 200 nm with image cross section.

Figure 6B presents the roughness profile in 3D AFM high resolution image, where the scanned area is 5 × 5 µm^2 and z-range is 200 nm.

The morphology of the chrome plated surface deposited on an aluminum alloy with 7 % silicon is presented as typical images with AFM height in 3D format, together with images of the optical microscope with 10x magnification showing the examined place and the respective area (Figure 6A and 6B).

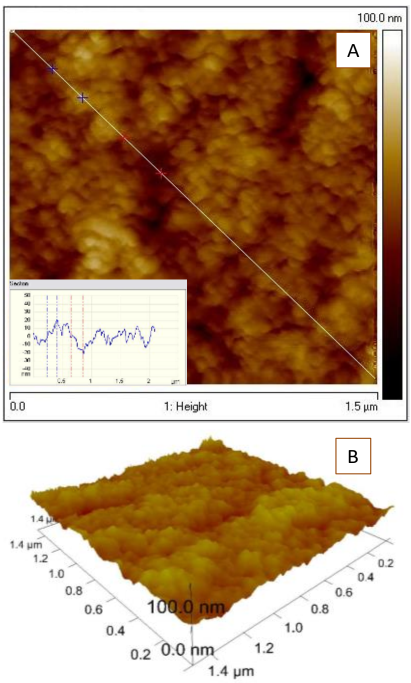

Fig.7. Topography of chromium coating with ND on aluminum alloy containing 10 % Si

The surface of chromium coatings with diamond nanoparticles deposited on aluminum alloys with silicon content of 7 % and 10 %, respectively, were examined by AFM. It was found that when the silicon content in the aluminum alloy increases, a presence of clusters with fine-grained structure on the surface of the chromium coating is observed (Figure 7). In general, the topography of the surface of the Cr ND/Al10Si coating is more smooth and more uniform (Figure 7), compared to the surface of the Cr ND/Al7Si coating shown in Figure 5 and Figure 6, which is more rough and more wavy.

Roughness is a very important surface property for technological applications. The applied roughness analysis of each AFM image uses values R_a, R_q and R_{max} calculated according to the relative heights of each pixel from the topography of the studied sample [7]. The roughness analysis gives the value R_a, which is an arithmetic average of the absolute values Z_j of the surface height deviations measured from the mean plane (1).

$$R_a = \frac{1}{N}\sum_{j=1}^{N} |Zj| \qquad (1)$$

while the image R_q is the root mean square average of height deviations taken from the mean image data plane (2) [5].

$$R_q = \sqrt{\frac{\sum_{j=1}^{N} Z_j^2}{N}} \qquad (2)$$

Table 1.
Morphology of the surface of the chromium coating deposited on aluminum alloy with 7 % and 10 % silicon

Sample	Roughness, R_a	Roughness, R_q	Roughness, R_{max}
Cr ND deposited on Al7Si with a step of 1.5 µm	15,4 nm	20,7 nm	183 nm
Cr ND deposited on Al7Si c with a step of 5 µm	14,8 nm	18.7 nm	134 nm
Cr ND deposited on Al10Si with a step of 1.5 µm	6,80 nm	8,63 nm	81,0 nm

Table 1 presents the data from the graphs of Figure 5A, Figure 5B and Figure 7A. These are the different types of roughness obtained by atomic force microscopy, which reveals that the deposition surface of Cr ND Al 7Si is twice (2.26) higher than the roughness of Cr ND Al 10Si at a scan area of 1.5 microns (2.25 µm^2). At the square roughness - Rq and at the maximum roughness - Rmax the ratio of about 2 times is preserved. These data prove that the coating follows the surface of the aluminum alloy (sample) and the smoother it is, the smoother is the coating. In our case, this is the chromium coating with ND deposited on an aluminum alloy with silicon content 10 %.

3.3. Wear resistance

The study was performed with a tribotester "Thumb-Disc" type which principal diagram is presented in [8].

The experimental samples are discs with diameter of 15 mm. The study was performed under the same friction conditions for all samples. The parameters of the experiment are presented in Table 2.

Table 2.
Experimental parameters of the wear study of the tested coatings

№	Parameters	Values
1	Normal load	P = 2.4 N
2	Nominal contact zone	A_a = 1.77 cm^2
3	Nominal contact pressure	P_a = 1.36 N/cm^2
4	Rotating speed	n = 212 min^{-1}
5	Distance between the axis of rotation and the center of the contact point	R_c = 37 mm
8	Sliding speed of the contact center site	V_c = 0.85 m/s
9	Ambient temperature	$T^o = 21^oC$
10	Abrasive surface	Corundum - N 500

The methodology for studying the wear characteristics consists in measuring the mass wear of the samples for a certain friction path (friction time) under constantly set conditions - load and sliding speed.
The methodology is in the following sequence:

– The mass of the sample m_o is measured with accuracy 0,1 mg. Before each measurement the sample is cleaned of mechanical and organic particles;
– The sample is placed in the load head holder, a predetermined normal load P and number of friction cycles (friction path) are set;
– Measurement of the mass of the sample m_i and the following wear characteristics are calculated:

Mass wear m - represents the difference in the mass of the sample before friction m_o and after a certain path / time of friction m_j:

$$m = m_o - m_i \text{ , [mg]} \quad (3)$$

Wear velocity - represents the destroyed mass of the surface layer of the sample at friction time t = 1 minute

$$\gamma = m/t \text{ , [mg/min]} \quad (4)$$

Wear rate i - represents the destroyed mass of the surface layer of the sample at a friction path S = 1 meter;

$$i = m/S \text{ , [mg/m]} \quad (5)$$

Wear resistance I - represents the resistance capabilities on wear of the surface layer/coating. It is presented as a reciprocal value of the wear intensity;

$$I = 1/i = S/m \text{ , [m/mg]} \quad (6)$$

The wear resistance shows how much friction path the sample will make in which a mass of 1 milligram will be released from its surface.
To compare the wear of the samples we chose the aluminum alloy with the higher microhardness of the matrix (Figure 4). This is an alloy with a higher content of silicon (Al10Si). Figure 8 presents the mass loss as a function of the number of cycles, respectively the sliding distance. With the least mass loss is the chromium coating deposited on the aluminum alloy with 7 % silicon - 2.6 mg, followed by the coating deposited on the alloy with 10 % silicon -3.8 mg and the uncoated sample - 12 mg at the maximum number of cycles – 250, respectively 53.4 m. The ratio of coated to uncoated samples is respectively: 12/3.8 = 3.2 times less mass loss when chromium with ND is deposited on aluminum alloy with silicon 7 % and 12/2.6 = 4.6 times less when chromium with ND is deposited on an aluminum alloy with silicon 10 %.

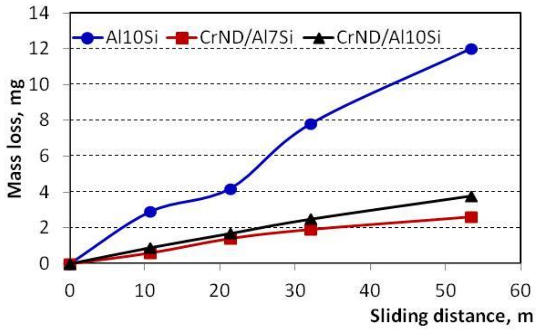

Fig. 8. Change of mass wear as function of sliding distance

Table 3 defines the characteristics of the coatings - wear rate, wear resistance and mass wear. The tendency is that sample 2 possesses the best performance. That is the chromium coating with diamond nanoparticles deposited on aluminum alloy with 7 % silicon.

Table 3.
Mass loss, wear rate and wear resistance of the test samples at 53.4 m friction path

Sample No	Empirical designation	Mass loss, mg	Wear rate, mg/m	Wear resistance, m/mg
1	Al10Si	12	22 $x10^{-2}$	4.5
2	Cr ND/Al7Si	2.6	4.9 $x10^{-2}$	20
3	Cr ND/Al10Si	3.8	7.1 $x10^{-2}$	14.1

The wear rate (Figure 9) passes through a sharp increase with a peak at 10 m, after which a decrease is observed with subsequent balancing of the curves until the end of the test.
The absolute wear resistance (Figure 10) maintains the same trend. The chromium coating with diamond nanoparticles deposited on an aluminum alloy with 7 % silicon possesses 1.42 times better absolute wear resistance than CrND/Al10Si coating and 4.44 times better than the uncoated one.Accordingly, the chromium coating with diamond nanoparticles deposited on an aluminum alloy with 10 % silicon is with 3.13 times better absolute abrasion resistance than the uncoated sample.

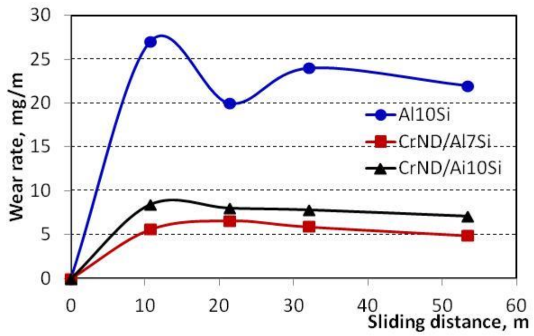

Fig. 9. Change of wear rate as function of sliding distance

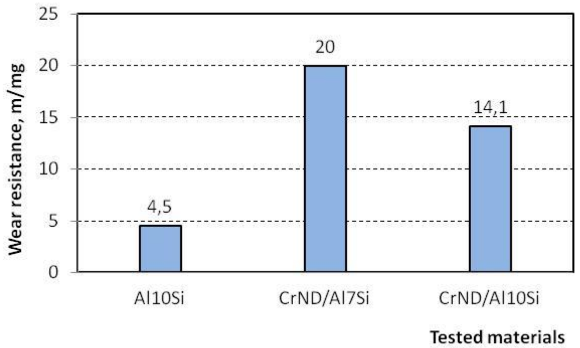

Fig.10. Diagram of the absolute wear resistance of the tested materials and coatings at sliding distance S=53.4 m

There is a visible correlation between the microhardness and wear resistance of chromium coatings deposited from electrolyte with a concentration of diamond nanoparticles 25 g/l. The best results being those deposited on an aluminum alloy with 7 % Si.
There is a tendency that with increasing the silicon content in the aluminum alloy the obtained chromium coatings are with slightly lower values of microhardness and wear resistance. It is very likely that this is due to the residual SiO_2 on the surface of the aluminum alloy, which hinders the deposition of the chromium coating.

4. Conclusions

- Electrochemical coatings of chromium with 25 g/l ND in the electrolyte were deposited directly without intermediate layers on aluminum alloys containing silicon (Si -7 % and Si -10 %), which is economically more effective
- It has been found that the coatings are dense, continuous and following the surface of the substrate with thicknesses of about 50 µm.
- It has been proven that the surface of CrND/Al10Si coating to be twice as smooth as that of CrND/Al7Si.
- It has been proven that the microhardness of the coated samples increases between 8-9 times compared to uncoated ones.
- It has been found that CrNDAl7Si coatings have the highest wear resistance, which is about 4.5 times higher than that of the uncoated samples and 1.4 times higher than CrNDAl10Si coatings.
- A proportional relationship was found between the microhardness and wear resistance of the chromium coating with 25 g/l of ND in the electrolyte deposited on aluminum alloys with Si – 7 %.
- The morphology of a chromium-coated surface with a ND deposited on aluminum alloy with Si - 7% and Si – 10 % respectively has been investigated by Atomic Force Microscopy (AFM). It has been found that when the silicon content increases in the composition of the alloy, clusters composed of individual grains are observed.

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