Аграрный научный журнал. 2023. №7. С. 159–165.
Agrarian Scientific Journal. 2023;(7):159–165.

АГРОИНЖЕНЕРИЯ

Научная статья
УДК 621.357
doi: 10.28983/asj.y2023i7pp159-165

Влияние наноразмерных частиц на физико-механические свойства гальванического цинка

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Аннотация. В статье представлены результаты исследования микротвердости и износостойкости гальванических покрытий на базе цинка, с включением в состав наноразмерных частиц Al_2O_3. Установлено, что при внесении наноразмерных порошков в электролиты цинкования, происходит изменение микротвердости и износостойкости. Так, при добавлении в электролит от 1 до 9 г/л наноразмерных материалов Al_2O_3, микротвердость получаемого покрытия увеличилась на 10–65 %. Лучшие результаты были у покрытия, модифицированного наноразмерными частицами с концентрацией 5 г/л – 657 единиц HV. Испытания на износостойкость показали, что суммарный износ образцов, покрытых нанокомпозиционным гальваническим цинком, в 1,5–1,7 раза меньше, чем образцов с покрытием без добавления наноразмерных частиц оксида алюминия в электролит.

Ключевые слова: нанокомпозиционное покрытие; гальваническое цинкование; наноразмерные частицы; оксид алюминия; микротвердость; износостойкость; момент трения.

Для цитирования: Горбушин П. А., Сафонов В. В., Шишурин С. А., Венскайтис В. В. Влияние наноразмерных частиц на физико-механические свойства гальванического цинка // Аграрный научный журнал. 2023. № 7. С. 159–165. http: 10.28983/asj.y2023i7pp159-165.

AGRICULTURAL ENGINEERING

Original article

Influence of nanosized particles on physical and mechanical properties of galvanic zinc coating

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Abstract. The article presents the results of a study of microhardness and wear resistance of electroplated coatings based on zinc, with the inclusion of Al_2O_3 nanosized particles in the composition. It has been established that when nano-sized powders are introduced into galvanizing electrolytes, there is a change in microhardness and wear resistance. Thus, when adding from 1 to 9 g/l of Al_2O_3 nanosized materials to the electrolyte, the microhardness of the resulting coating increased by 10–65 %. The best results were obtained for the coating modified with nanosized particles with a concentration of 5 g/l – 657 HV units. Wear resistance tests showed that the total wear of specimens coated with nanocomposite galvanized zinc is 1.5–1.7 times less than that of specimens coated without adding nanosized aluminum oxide particles to the electrolyte.

Keywords: nanocomposite coating; galvanic zinc plating; nanosized particles; aluminum oxide; microhardness; wear resistance; friction moment.

For citation: Gorbushin P. A., Safonov V. V., Shishurin S. A., Venskaitis V. V. Influence of nanosized particles on physical and mechanical properties of galvanic zinc coating // Agrarnyy nauchnyy zhurnal = The Agrarian Scientific Journal. 2023;(7):159–165. (In Eng.). http: 10.28983/asj.y2023i7pp159-165.

Introduction. At present, galvanic coatings are widely used in various industries. Among them, a special place is occupied by galvanic coatings based on zinc, obtained from zinc alkaline electrolytes [1]. Their advantages include high productivity of the coating process, its cost-effectiveness, no thermal effect on the deposited surface and high corrosion resistance of the resulting coating [2]. However, despite all the advantages of coatings, they are not without significant drawbacks, namely, unsatisfactory indicators of microhardness and wear resistance. For further widespread use of these coatings, it is proposed to eliminate these shortcomings by modifying galvanizing electrolytes with nanosized materials ranging in size from 10 to 100 nm. However, the authors of [1, 2, 4] found that the type of nanosized materials, their concentration in the electrolyte and chemical composition does not unambiguously affect the physical and mechanical properties of electroplated coatings. In connection with the foregoing, it is proposed to study the effect of Al_2O_3 nanopowder on the microhardness and wear resistance of galvanized zinc.

Materials of research. For research, a nanocomposite galvanic coating was applied to the samples from an electrolyte of the following composition [1]:

zinc chloride State Standard 4529-78 ($ZnCl_2$): 20–30 g/l;

sodium hydroxide State Standard R 55064-2012 (NaOH): 100–120 g/l;

Electrolysis modes:

cathodic current density: 4 A/dm^2;

electrolyte temperature: 18 °C.

time of coating deposition: 10 min under the action of a current of direct polarity.

Analysis of existing technologies for creating nanoscale materials for galvanic coatings modification made it possible to choose the method of plasma recondensation, which produces powders of various metals with particle sizes from 10 to 100 nm [6, 7].

When choosing a material for nanoscale powder for modifying galvanic zinc coatings, the following requirements are followed:

powder particles must have high hardness to increase the microhardness of the coating;

powder particles must be chemically resistant to galvanizing electrolyte and have good wettability;

Based on the results of previous studies of the authors, literature sources in the field of composite coatings, as well as to meet the requirements for particles, a nano-sized alumina powder (Al_2O_3) was chosen at a concentration of 1 to 9 g/l [3, 6–12].

The electrolyte suspension for obtaining zinc coatings was prepared in several stages. A concentrated suspension was prepared to disaggregate the particles and increase the sedimentation stability of the electrolyte. The prescription amount of nanosized particles was preliminarily poured with electrolyte and, by grinding them for 10 min, the suspension was brought to a pasty state. Then, an additional electrolyte was added to the mixture, and a concentrated suspension was obtained, which was further processed using an UZG-2M ultrasonic generator with a frequency of 22 kHz and an amplitude of 50 Hz for 10–12 min. Then the resulting suspension was introduced into a galvanizing bath with intensive mechanical stirring of the electrolyte. Preparation of the surface of the part for the application of coatings included degreasing and pickling [7, 12].

The part was degreased in a 10 % sodium hydroxide solution State standard R 55064-2012 (NaOH). Processing mode:

electrolyte temperature: 50 °C;

cathode current density: 20 A/dm^2;

the operation time is 5 minutes under the action of direct polarity current.

After degreasing, the samples were washed successively in hot (70–80 °C) and running water at room temperature for 1–2 min.

When preparing the samples for coating, they were pickled in order to remove corrosion products, scale and fatty films from the surfaces in a solution of the following composition:

sulfuric acid of State standard 2184-2013 (H_2SO_4): 150 g/l;

hydrochloric acid of State standard 3118-77 (HCl): 150 g/l.

Processing mode:

electrolyte temperature: 30 °C;

etching time: 1 min.

After pickling, the part was washed in running water at room temperature for 1–2 min.

To maintain a given concentration of components, the electrolyte was corrected by introducing new portions of the components into it in accordance with the well-known technique [7].

The samples were coated using laboratory galvanic equipment (fig. 1).

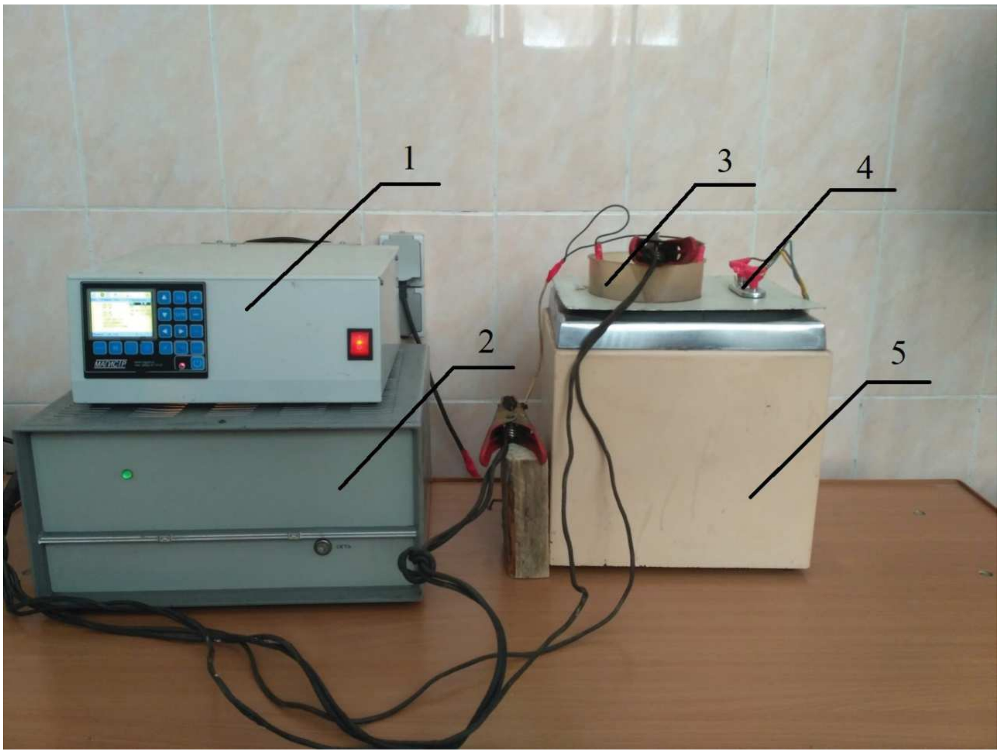

Fig. 1. Laboratory galvanic equipment: 1 – rectifier GITP 500 – 30 (5) x12R – 220 – P2 / B2; 2 – power supply unit for the ultrasonic bath; 3 – electrolyte container; 4 – heating element; 5 – ultrasonic bath

Test coating was applied to the samples in the form of plates made of medium-carbon steel 40 State standard 1050-2013 with dimensions of 100x20x2 mm according to the method described above. The microhardness was measured on a Durascan 20 microhardness tester, according to State standard 9450-76, using the restored indentation method [5, 8, 9]. To obtain the most accurate results of measuring microhardness, the latter should be measured on metallographic sections. In this case, the indenter of the measuring device will be pressed directly into the coating, avoiding the influence of the microhardness of the base of the sample. Samples were prepared using a Labotom 5 cutting machine and a Struers CitoPress-1 electro-hydraulic press to form a section and obtain a correct surface end.

After obtaining a cut at the end of the section, it was ground and polished using an MDG02 double-disk grinder and a Struers TegraPol-15 grinder and polisher.

To obtain a distinct boundary between the metal layers, after polishing, sections were etched in a reagent of the following composition:

hydrochloric acid of State standard 3118-77 (HCl): 50 ml;

ethyl alcohol of State standard R 56389-2015 (C_2H_5OH): 100 ml.

Processing mode:

reagent temperature: 50 °C;

etching time: 1 min.

The measurement of the wear resistance of the obtained coatings was carried out under sliding friction on an SMTs-2 friction machine (fig. 2), the contacting of the samples was carried out according to the “roller-pad” scheme (fig. 3).

To obtain more accurate values, 3 friction pairs were tested. The coating was applied to samples in the form of rollers made of steel 45 State standard 1050-2013 with a diameter of 50 mm and a width of 10 mm. The surface of the rollers was ground to obtain a roughness of Ra 0.32 μm.

The pads were also made of steel 45 of State standard 1050-2013 with an outer diameter of 68 mm, the inner diameter of which was ground to fit the size of the roller and polished to a roughness of R_a 0.32 μm. The pads were not coated. The tests were carried out in accordance with State standard 23.224-86 in two environments: in a clean and contaminated industrial oil I-20 of State standard 20799-88.

Fig. 2. Friction machine SMTs-2

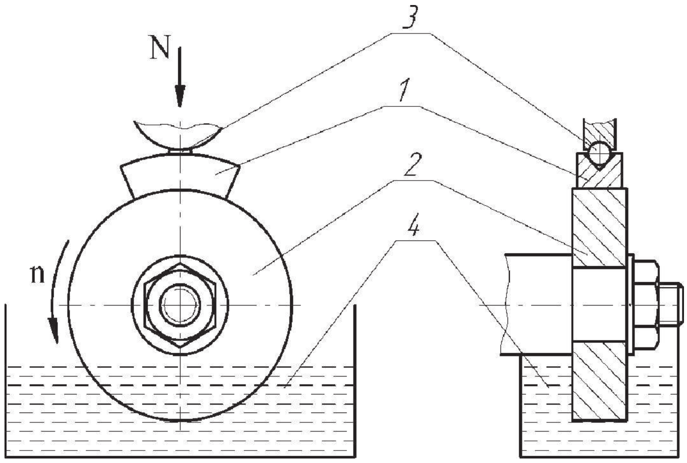

Fig. 3. Scheme «roller – pad»: 1 – pad; 2 – roller; 3 – pad retainer; 4 – lubricating medium

Quartz abrasive 1K1O101 of State standard 2138-91 with a particle size of 8–12 μm at a concentration of 0.08 % by weight was the pollutant. The test modes of the corresponding friction pairs are presented in Tab. [7].

Test modes for wear resistance

Test name	Load, N	Roller rotation frequency, min^{-1}	Lubricating environment	Test duration, h
Running-in	850	500	I-20 oil	1
Testing in a clean lubricating environment	850	500	I-20 oil	3
Testing in a contaminated lubricating environment	850	500	I-20 oil contaminated with abrasive	3

In order to form the initial microgeometry and structure of the working surfaces, the samples of friction pairs were subjected to running-in before testing in the modes shown in Tab.

During the tests, the frictional moment in the test pair was recorded. The wear of the samples was determined by weighing them before and after testing on an HR-250AZG balance.

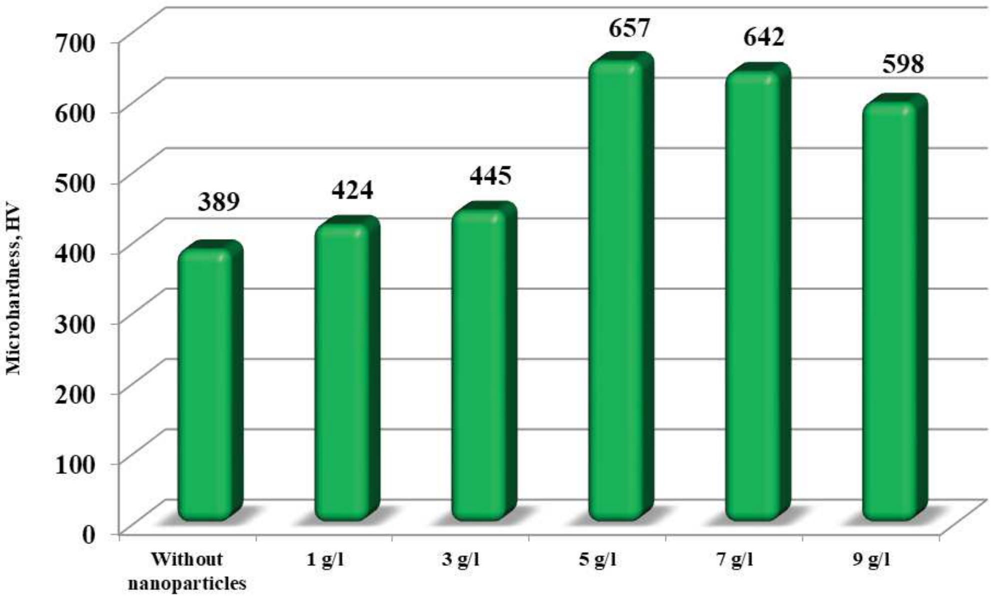

Fig. 4. Histogram of the microhardness of the nanocomposite zinc coating depending on the concentration of nanosized particles in the electrolyte

Research results. The analysis of the results of measuring the microhardness of the nanocomposite zinc coating is based on the assumption of the heterogeneity of the phase composition of the coatings, the presence of pores and defects, and measurement errors; therefore, the microhardness was considered as the average value of three dimensions of indentations for each sample. The microhardness results are presented in the histogram in Fig. 4.

From the presented data, it can be seen that when modifying the galvanic coating of zinc with nanosized particles of aluminum oxide, the highest microhardness value of 657 HV units is achieved at a concentration of nanosized particles in the electrolyte equal to 5 g/l.

In this regard, when testing for wear resistance, we used samples coated with galvanic zinc without the addition of nanosized particles and samples coated with galvanic zinc with the addition of nanosized Al_2O_3 particles with a concentration of 5 g/l. The results of testing samples for wear resistance are presented in Fig. 5 and 6.

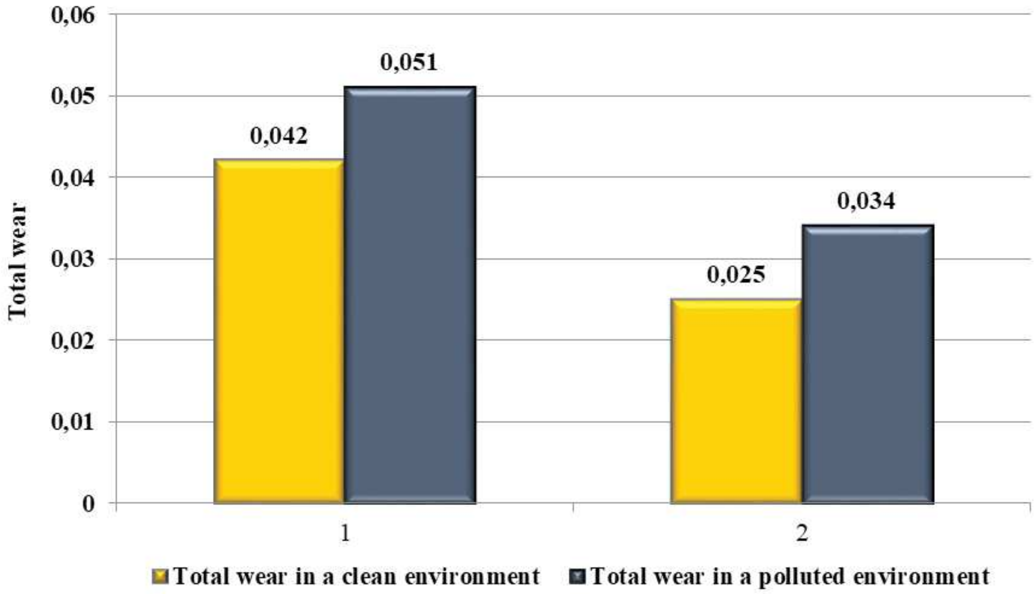

Fig. 5. Total wear of friction pairs with zinc coating after wear resistance tests: 1 - without adding nanosized particles; 2 - with the addition of nanosized Al_2O_3 particles

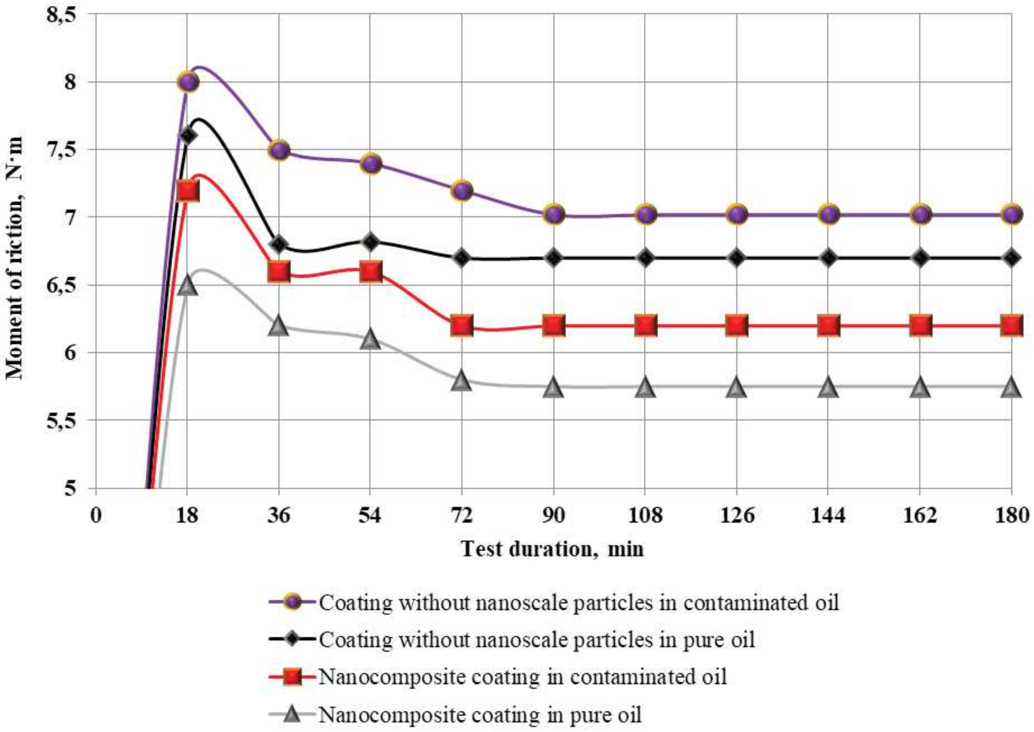

Fig. 6. Change in friction moment during wear resistance tests

Fig. 5 shows that the least wear was observed for a friction pair, where the rollers were coated with a nanocomposite coating, both when tested with pure I-20 oil and when tested with contaminated oil.

When tested in pure oil, the total wear of the friction pairs on the rollers of which the nanocomposite coating was applied was 0.025 g, while for the friction pairs, on the rollers of which the coating was applied without nanosized particles, the wear was 0.042 g, which is 1.7 times more.

In contaminated oil, the total wear of the friction pairs, on the rollers of which the nanocomposite coating was applied, was 0.034 g, and in the friction pairs, on the rollers of which the coating was applied without nanosized particles, it was 0.051 g, which is 1.5 times more.

During the wear tests, a change in the frictional moment was recorded (see Fig. 6). So, for friction pairs with a nanocomposite coating operating on I-20 pure oil, the friction moment by the end of the tests was 5.75 N·m, while for friction pairs with a coating without nanosized particles, the friction moment was 6.7 N·m, which is 16.5 % higher.

When tested on I-20 contaminated oil, the friction moment for samples with a nanocomposite coating by the end of the tests was 6.2 N·m, and for friction pairs with a coating without nanosized particles it was 7.02 N·m, which is 13 % higher.

Zinc-based galvanic coatings are widely used in various industries to protect metal surfaces from corrosion, however, the low microhardness and wear resistance of such coatings seriously limit their use in other areas. At the same time, zinc-based galvanic coatings have a number of advantages compared to other types of coatings. These are low cost, ease of application process, high current efficiency and the like. To expand the scope of zinc coatings, including for restoring the working surfaces of parts of various assemblies and assemblies, it was suggested that the modification of such coatings with hard nanoscale materials can increase the microhardness and wear resistance of zinc coatings.

For modification, various nanosized powders were considered, preliminary tests were carried out with them, however, the final decision remained with the use of Al_2O_3 nanosized particles, since particles of this material, when modifying electroplated coatings, increase hardness and wear resistance, including under conditions of dry friction and elevated temperatures, heat resistance, corrosion resistance and strength of the latter. At the same time, unlike carbides and nitrides, oxides are more heat-resistant and under normal conditions do not decompose and do not turn into other compounds.

During the deposition of zinc-based nanocomposite coatings, in addition to increasing microhardness and wear resistance, it was found that its surface does not chip as a result of interaction with the mating body, which may be the result of a decrease in the number of pores due to the uniform distribution of nanosized particles in the coating.

Conclusion. The studies indicate that when modifying galvanic coatings based on zinc with nanosized particles of aluminum oxide, the most effective concentration of these particles in the electrolyte is 5 g/l, which makes it possible to obtain coatings with a microhardness of up to 657 HV. Tests for wear resistance showed that the total wear of friction pairs, the rollers of which were coated with a nanocomposite coating, is 1.5–1.7 times less than that of friction pairs, the rollers of which were coated with zinc without nanosized particles. At the same time, a friction moment in friction pairs with a nanocomposite coating is 13–16.5 % lower than that of friction pairs with a coating without nanosized particles. Based on this, it can be concluded that nanocomposite galvanic coatings based on zinc are promising for use in various industries where it is necessary to create a layer with high hardness, corrosion resistance, and tribological properties on the surface of parts.

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Статья поступила в редакцию 30.03.2023; одобрена после рецензирования 15.04.2023; принята к публикации 30.04.2023.

The article was submitted 30.03.2023; approved after reviewing 15.04.2023; accepted for publication 30.04.2023.