STUDY OF WEAR RESISTANCE AND NANOSTRUCTURE OF TERTIARY Al_2O_3/Y_2O_3/CNT PULSED ELECTRODEPOSITED Ni-BASED NANOCOMPOSITE

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Electrodeposition of tertiary Alumina/Yitria/carbon nanotube (Al_2O_3/Y_2O_3/CNT) nanocomposite by using pulsed current has been studied. Coating process has been performed in nickel sulphate bath and nanostructure of the obtained compound layer was examined with high precision figure analysis of SEM nanographs. The effects of process variables, i.e. Y_2O_3 concentration, treatment time, current density and temperature of electrolyte have been experimentally studied. Statistical methods were used to achieve the minimum wear rate and average size of nanoparticles. Finally the contribution percentage of different effective factors was revealed and confirmation run showed the validity of the obtained results. Also it has been revealed that by changing the size of nanoparticles, wear properties of coatings will change significantly. Atomic force microscopy (AFM) and transmission electron microscope (TEM) analysis have confirmed smooth surface and average size of nanoparticles in the optimal coating.

Key words: *yitria, electrodeposition, tertiary nanocomposite coatings, wear, carbon nanotube.*

Nickel and nickel-based alloys are used widely for numerous applications, which most of them require corrosion, wear and heat resistances, including different turbine plants, nuclear power systems, and chemical and oil industries.

Ceramic or metal matrix nanocomposite coatings usually have special properties such as dispersion hardening, self-lubricity, high temperature inertness, good wear and corrosion resistance, chemical and biological compatibility [1–7]. This accounts for the increased application of Ni-based nanocomposites in different industries. In order to meet the requirement for developing novel metal-based nanocomposites, many preparation techniques have been investigated. Considering a technique conducted at a normal pressure and ambient temperature and with low cost and high deposition rate, electrodeposition is considered to be one of the most important techniques for producing nanocomposites and nanocrystals [8–11].

In this paper, tertiary nanocomposite coatings consisting of nanometric-sized Al_2O_3/Y_2O_3/CNT particles embedded in a Ni-matrix by pulsed electrodeposition method were studied. The nanostructure and wear resistance of obtained nanocomposites were investigated with respect to the different effective factors of coating process. Ni matrix composite coatings containing nano-sized Al_2O_3/Y_2O_3/CNT fine particles with different average sizes of nanoparticles were prepared in a nickel sulphate bath. The wear performance of these coatings and its relation to the distribution of nanopaticles has been analyzed in a systematical way.

The design of experiment (Taguchi method) [12–13] took into account the influencing extent of individual process parameter. This consideration led to the selection of four influential factors, i.e. Y_2O_3 concentration, time, current density and

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temperature of electrolyte with three different levels (1–3). Figure analysis measurements were conducted to determine the size of nanocrystals of the coated samples. The results of the factor response analysis were used to derive the optimal levels combinations. Confirmation experiments were performed to verify the analytical results. The percentage contribution of each factor was determined by the variance analysis.

Experimental procedure. ***Materials and treatments.*** Electrodeposition nickel sulphate bath is composed of pure 150 g/L $NiSO_4$-$7H_2O$, 15 g/L NH_4Cl, 15 g/L H_3BO_3, 0.1 g/L $C_{12}H_{25}NaSO_4$, with 0.01 g/L saccharin ($C_7H_5NO_3S$), 0.01 g/L SDS ($C_{12}H_{25}NaO_4S$) and 0.1 g/L CNT nanoparticles, 50 g/L $Al_2O_3(X\%)Y_2O_3$ ($X = 2, 6, 10$). Pure copper 50×50×1 mm sheets were used as cathodic electrodes. The preparing process for all specimens was the following: first they were mechanically polished with different grade emery papers up to #3000 and then degreased in sodium hydroxide solution, after that inserted in 10% HCl solution to be activated and finally rinsed with acetone. The operating conditions for plating were such: average current density equal to 10 A/dm^2, stirring rate 200 rpm and bath temperature 60°C while the frequency and duty cycle of monopolar pulsed current were adjusted at 1000 Hz and 50%.

Evaluation of coatings. After coating process, samples were rinsed thoroughly with distilled water and then dried in flowing air. The microstructure of surfaces and cross-section of the samples were examined by a Philips XL-30 scanning electron microscopy (SEM). The wear rate of the coatings was evaluated using the standard pin on the disc wear test. The sample weight was measured every 100 m of sliding distance and wear rate was calculated from obtained data using Archard equation. Sample weight after wear tests was measured by Sartorious CP324S digital scale. To measure an average size of nanoparticles (ASN), 5 SEM nanostructures with the same magnification were analyzed trough commercial software for figure analysis called a4iDocu for each treated sample. Different measurements were interpolated to obtain average results. At least 40 measurments were done in each nanostructure for minimizing systematical errors. Nanostructure of optimal layer was studied with AFM and TEM. AFM part was a NanoScope II from Digital Instruments, USA and non-scraping Si_3N_4-tips were used throughout. TEM analysis was done on a JEM-2000EX with 200 KV of bias voltage.

Statistical analysis. *Design of orthogonal array and signal-to-noise analysis.* Four Taguchi independent factors (Y_2O_3 concentration, time, current density and temperature of electrolyte) with three levels were selected (Table 1). The factors and levels were used to design an orthogonal array L_9 (3^4) for experiments. The nine Taguchi experiments were conducted twice to ensure the reliability of experimental data for a signal-to-noise analysis. In process design, it is almost impossible to eliminate all errors caused by the variation of characteristics. An increase in the variance of wear rate and nanoparticles average size lowers the quality reliability of coatings. To minimize the influence of wear rate and average size of nanoparticles variation on the analysis of experimental data, the signal-to-noise (S/N) ratio was employed, which converts the trial result data into a value for the response to evaluate coating quality in the optimum setting analysis. The S/N ratio consolidates several repetitions into one value which reflects the amount of variation present. This is because the S/N ratio can reflect both the average and the variation of the quality characteristics. There are several S/N ratios available depending on the types of characteristics [12]: lower is best (LB), nominal is best (NB), and higher is best (HB). In the present study wear rates and average sizes of nanoparticles are treated as characteristic values. Since the wear rate and average size of nanoparticles of coatings intended to be minimized, the S/N ratio for LB characteristics was selected which can be calculated as follows:

$$S/N_{\mathrm{LB}} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} X_i^2\right), \tag{1}$$

where n is the repetition number of each experiment under the same condition for design parameters, and X_i is the wear rate or the average size of nanoparticles for individual measurement at the ith test. After calculating and plotting the mean S/N ratios at each level for various factors the optimal level, that is the lowest S/N ratio among all levels of the factors, can be determined.

Table 1. Design factors and levels

Level	Factor			
	Y_2O_3, %	t, min	i, A/cm^2	T, °C
1	2	10	0.02	40
2	6	20	0.06	50
3	10	30	0.1	60

Analysis of variance (ANOVA). The ANOVA analysis of the experimental results was performed to evaluate the source of variation during the electrodeposition. Following the analysis it is relatively easy to identify the effect order of factors on coatings and the contribution of factors to the wear rate and average size of nanoparticles in coatings. In this study variation due to both the four factors and the possible error was taken into consideration. The ANOVA was established based on the sum of the square (*SS*), the degree of freedom (*D*), the variance (*V*), and the percentage of the contribution to the total variation (*P*). The five parameters symbols typically used in ANOVA [13] are described below:

1. *Sum of squares (SS)*. SS_p denotes the sum of squares of factors *A*, *B*, *C*, and *D*; SS_e is the error sum of squares; SS_T is the total sum of squares. The total sum of square SS_T from S/N ratio can be calculated as:

$$SS_T = \sum_{i}^{m} \eta_i^2 - \frac{1}{m}\left[\sum_{i=1}^{m} \eta_i\right]^2, \tag{2}$$

where m is the total number of the experiments, and η_i is the S/N ratio at the i-th test. The sum of squares from the tested factors, SS_P, can be calculated as:

$$SS_P = \sum_{j=1}^{p} \frac{(S_{\eta_j})^2}{t} - \frac{1}{m}\left(\sum_{i=1}^{m} \eta_i\right)^2, \tag{3}$$

where p represents one of the tested factors; j is the level number of this specific factor p; t is the repetition of each level of the factor p; and S_{η_j} is the sum of the S/N ratio involving this factor and level j.

2. *Degree of freedom (D)*. *D* denotes the number of independent variables. The degree of freedom for each factor (D_P) is the number of its levels minus one. The total degrees of freedom (D_T) is the number of total number of the result data points minus one, i.e. the total number of trials times number of repetition minus

one. The degree of freedom for the error (D_e) is the number of the total degrees of freedom minus the total of degree of freedom for each factor.

3. *Variance (V).* Variance is defined as the sum of squares of each trial sum result involved in the factor, divided by the factor degrees of freedom:

$$V_P(\%) = \frac{SS_P}{D_P} \times 100 . \quad (4)$$

4. *The corrected sum of squares* (SS'_P). SS'_P is defined as the sum of squares of factors minus the error variance times the degree of freedom of each factor:

$$SS'_P = SS_P - D_P V_e . \quad (5)$$

5. *Percentage of the contribution to the total variation (P).* P_P denotes the percentage of the total variance of each individual factor:

$$P_P(\%) = \frac{SS'_P}{SS_T} \times 100 . \quad (6)$$

Determination of relationship to nanostructure. After determining optimal levels, the changes (increasing/decreasing) of results with average size of nanoparticles have been determined and the regressed plots show these relations. Obtained formula from interpolating different achieved data for effective factors with $R_{\text{fitt}} \geq$ ≥ 0.98 which shows excellent fittings have been determined beside the trend of changing in relative figures and plots.

Results and discussions. ***Effect of coating effective parameters.*** Based on equation (1), two wear rates and average sizes of nanoparticles measurements for each experiment were converted into one *S*/*N* ratio. In the following discussion the *S*/*N* ratios are employed as a response index to compare the wear rates and average sizes of nanoparticles for different coatings instead of directly using their values. The response of each factor to its individual level was calculated by averaging the *S*/*N* ratios of all experiments at each level for each factor. The determined factor responses are summarized in Table 2. Fig. 1 shows the effect of the four effective factors on the mean *S*/*N* ratios for wear rates as well as Fig. 2 – average sizes of nanoparticles.

Table 2. The *S*/*N* ratios

Experiment, №	Y_2O_3, %	*t*, min	*i*, A/cm^2	*T*, °C	current density, mm^3/N·m·10^{-5}		*S*/*N*	average *d*, nm		*S*/*N*
					Test 1	Test 2		Test 1	Test 2	
1	1	1	1	1	25.5	24.8	28.01	159	155	43.92
2	1	2	2	2	13.7	14.4	22.96	86	90	38.89
3	1	3	3	3	10.8	11.4	20.91	67	71	36.78
4	2	1	2	3	5.5	6	15.20	34	38	31.14
5	2	2	3	1	3.5	3.1	10.39	22	19	26.26
6	2	3	1	2	14.3	13.9	22.99	90	87	38.94
7	3	1	3	2	4.9	5.5	14.33	30	34	30.12
8	3	2	1	3	7	6.5	16.59	44	40	32.47
9	3	3	2	1	3.8	3.3	11.03	24	20	26.88

The response of the S/N ratio to the Y_2O_3 concentration, treatment time, current density and temperature of electrolyte need to be further investigated. By selecting the lowest value of mean S/N ratio for each factor, the optimal level can be determined. On this basis, the optimum combination of levels in terms of minimizing the wear rates and average sizes of nanoparticles for coated samples is A2B2C3D1; i.e. 6% for Y_2O_3 concentration, 20 min for treatment time, 0.1 A/cm^2 for current density and 40°C for temperature of electrolyte. Also the optimum combination of levels in terms of minimizing the wear rates and average sizes of nanoparticles for coated samples is equal for both of wear rates and average sizes of nanoparticles which clearly show that decreasing the average sizes of nanoparticles will lead to lower wear rates of samples.

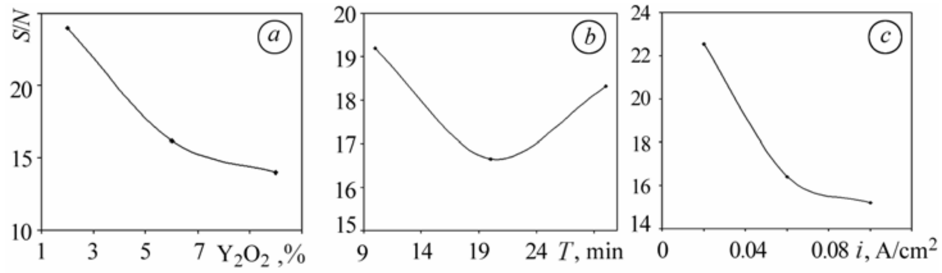
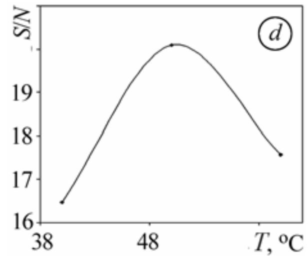


Fig. 1. Effect of Y_2O_3 concentration (*a*), treatment time of electrolyte (*b*), current density (*c*) and temperature of electrolyte (*d*) on mean S/N ratio for wear rate.



Factor contributions. The contribution of each factor to the wear rates and average sizes of the nanoparticles of coatings can be determined by performing analysis of variance based on Eqs. (2)–(6). The results of ANOVA are summarized in Table 3. The data given in Tables 4 and 5 show that the contribution of the four factors for wear rate, i.e. Y_2O_3 concentration, treatment time, current density and temperature of electrolyte is 57.2%, 3.46%, 32.16% and 7.17%, respectively. The contribution of Y_2O_3 concentration (57.2%) is more than the sum (42.8%) of the contributions of all the other three factors. It is evident that among the selected factors Y_2O_3 concentration has the major influence on the wear rate of performed coatings. It can be seen that the current density is the second important factor that affects the wear rate of the treated substrates. Furthermore, it can be assumed that treatment time and temperature of electrolyte have almost the same effect on wear rates of coatings because of the minor difference in the contribution percentages between these two factors. It is evident from Tables 4, 5, and 6 that ANOVA analysis not only specifies how important a factor is to the coatings wear rate by numbers but also shows their relative effect. By ranking their relative contributions the sequence of the four factors affecting the wear rate is Y_2O_3 concentration, current density, treatment time and temperature of electrolyte. Tables 5, 6 show the contribution of the four factors for average sizes of nanoparticles, i.e. 57.15%, 3.38%, 32.32% and 7.14%, respectively for Y_2O_3 concentration, treatment time, current density and temperature of electrolyte. As mentioned in the previous section, changes of wear rates and average sizes of nanoparticles of coatings with respect to different effective factors demonstrate similar trends which show strong relation between average sizes of nanoparticles and wear rates of coatings. It is also worthwhile mentioning that in the ANOVA analysis, if the percentage error (P_e) contribution to the total variance is lower than 15%, no important factor is missing in the experimental design. In contrast, if the percent contribution of the error exceeds 50%, certain significant factors have been overlooked and the experiments must be re-designed [12].

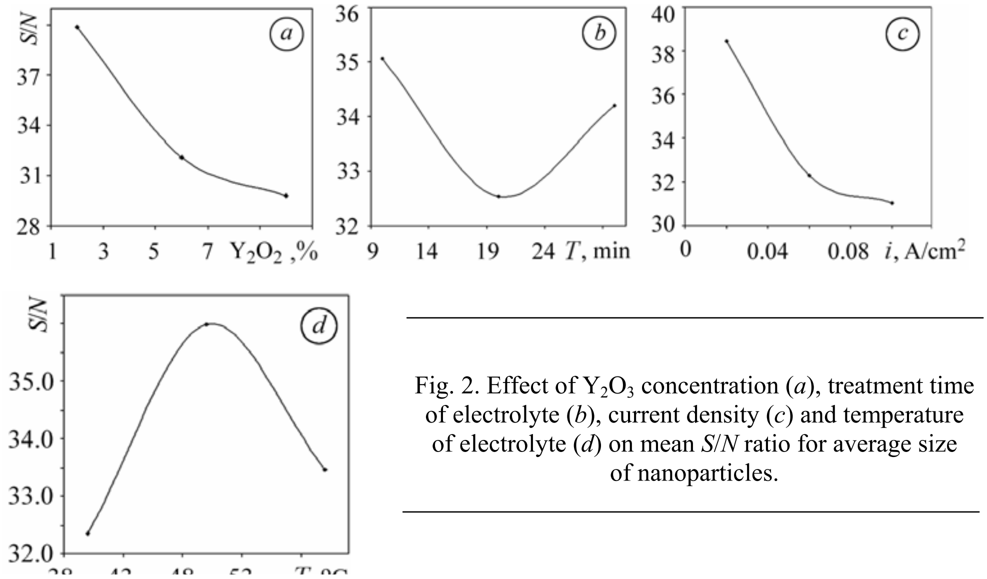


Fig. 2. Effect of Y_2O_3 concentration (*a*), treatment time of electrolyte (*b*), current density (*c*) and temperature of electrolyte (*d*) on mean *S*/*N* ratio for average size of nanoparticles.

Table 3. The factor response

Level	Factor			
	Y_2O_3, %	*t*, min	*i*, A/cm^2	*T*, °C
1WR	23.959	19.183	22.530	16.475
2WR	16.191	16.645	16.395	20.092
3WR	13.984	18.307	15.210	17.568
1ASN	39.864	35.059	38.445	32.354
2ASN	32.113	32.542	32.305	35.984
3ASN	29.826	34.202	31.053	33.465

As shown in Tables 4 and 5 the percentage error (P_e) is 0%. This indicates that no significant factors are missing in the experimental design.

Table 4. Results of the ANOVA for wear rate

Symbol	Factors	*D*	*SS*	*V*	*SS'*	*P*, %	Rank
A	Y_2O_3,%	2	164.7139	82.3569	164.7139	57.20	1
B	*t*, min	2	9.9695	4.9847	9.9695	3.46	4
C	*i*, A/cm^2	2	92.6168	46.3084	92.6168	32.16	2
D	*T*, °C	2	20.6522	10.3261	20.6522	7.17	3
Error		9	0	0		0	
Total		17	287.9524			100	

Table 5. Results of the ANOVA for average size of nanoparticles

Symbol	Factors	*D*	*SS*	*V*	*SS'*	*P*, %	Rank
A	Y_2O_3, %	2	166.0571	83.0285	166.0571	57.15	1
B	*t*, min	2	9.83	4.9150	9.83	3.38	4
C	*i*, A/cm^2	2	93.8957	46.9478	93.8957	32.32	2
D	*T*, ºC	2	20.7591	10.3795	20.7591	7.14	3
Error		9	0	0		0	
Total		17	1056.2004			100	

Confirmation run. The confirmation experiment is the final step in verifying the conclusions from the previous round of experimentation. If the results of the confirmation runs are not consistent with the expected conclusions, a new Taguchi method design is required. The confirmation experiment was performed by setting the experimental condition of the four factors: 6% for Y_2O_3 concentration, 20 min for treatment time, 0.1 A/cm^2 for current density and 40°C for temperature of electrolyte for the minimum wear rate and average size of nanoparticles. Table 6 gives the detailed results from the confirmation run on the optimized coating. Fig. 3 shows the SEM nanostructure of the coated samples from the confirmation run. The size of nanoparticles of the optimized coating is about 19 nm, which is the lowest value among other coatings obtained in the present study. During this study it has been revealed that by lowering the average size of nanoparticles, the wear rate of a compound layer will improve significantly. Fig. 4 shows this modification for different coatings. Figures 5 and 6 illustrate smooth surface of optimal coating after confirmation run and confirm the average size of nanoparticles with minimum roughness on the surface.

Table 6. Results of wear rate and average size of nanoparticles for confirmation run (optimal coating)

Experiment	Y_2O_3, %	*t*, min	*i*, A/cm^2	*T*, °C	*v*, mm^3/N·m ·10^{-5}	*d*, nm
Optimal coating	6	20	0.1	40	3	19

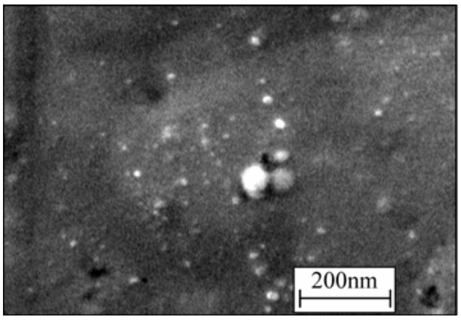


Fig. 3.

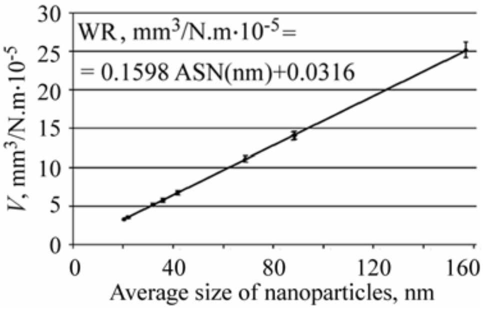


Fig. 4.

Fig. 3. SEM nanostructure of optimal coating.

Fig. 4. Relation between average size of nanoparticles and wear rate.

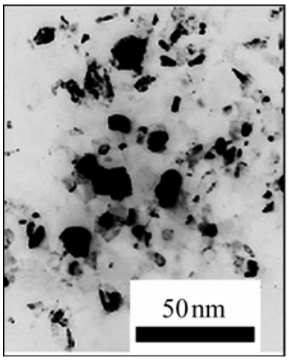


Fig. 5.

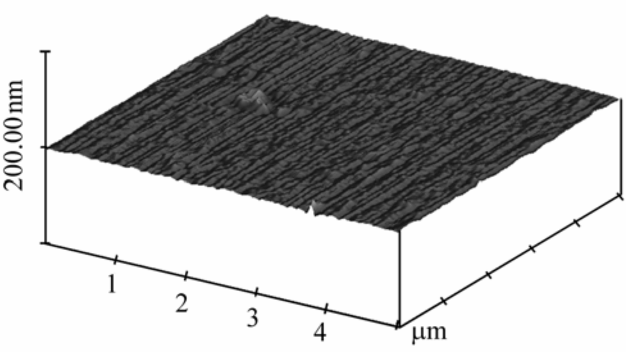


Fig. 6.

Fig. 5. TEM (BFI) nanostructure of optimal coating.

Fig. 6. AFM nanostructure of optimal coating.

CONCLUSIONS

The Taguchi method for the design of experiment has been used for optimizing tertiary (Al_2O_3/Y_2O_3/CNT) nanocomposite electrodeposited coating process parameters for wear protection of treated samples. The contribution of Y_2O_3 concentration is more than the sum of the contributions of all the other three factors. It is evident that among the selected factors Y_2O_3 concentration has the major influence on the wear rate of performed coatings. It can be seen that the current density is the second important factor that affects the wear rate of the treated substrates. Furthermore it can be assumed that treatment time and temperature of electrolyte have almost the same effect on wear rates of coatings because of the minor difference in the contribution percentages between these two factors. By ranking their relative contributions the sequence of the four factors affecting the wear rate is Y_2O_3 concentration, current density, treatment time and temperature of electrolyte. In the case of average size of nanoparticles, ranking of effective factors by their relative contributions is the same as for wear rate which shows strong relation between these two measured properties of coatings. AFM and TEM analysis have confirmed smooth surface and average size of nanoparticles in the optimal coating.

РЕЗЮМЕ. Вивчено електроосадження методом імпульсного струму потрійного композиту на основі вуглецевих нанотрубок, алюмінію та ітрію оксидів. Покриви наносили у нікелесульфатній ванні, а наноструктуру отриманого складного шару досліджували методом комп'ютерного аналізу знімків, одержаних на електронному мікроскопі. Вплив змінних параметрів процесу, зокрема, концентрації Y_2O_3, часу обробки, густини струму та температури електроліту вивчали експериментально. Для мінімізації впливу відхилень швидкості зношування та середнього розміру наночастинок на аналіз експериментальних даних використовували статистичні методи. Встановлено процентний вклад різних факторів і виконано підтверджувальний розрахунок, який показав достовірність одержаних результатів. Також виявлено, що зміна розміру наночастинок та зносотривкість покривів матиматимуть значною мірою однаковий тренд.

РЕЗЮМЕ. Изучено электроосаждение методом импульсного тока тройного композита на основе углеродных нанотрубок, алюминия и иттрия оксидов. Покрытия наносили в никельсульфатной ванне, а наноструктуру полученного сложного слоя исследовали методом компьютерного анализа снимков, полученных на электронном микроскопе. Влияние изменяющихся параметров процесса, в частности, концентрации Y_2O_3, времени обработки, плотности тока и температуры электролита изучали экспериментально. Для минимизации влияния отклонений скорости изнашивания и среднего размера наночастиц на

анализ экспериментальных данных использовали статистические методы. Установлен процентный вклад разных факторов и проведен подтверджающий расчет, который показал достоверность полученных результатов. Также установлено, что изменение размера наночастиц и износостойкость покрытий имеют в значительной степени одинаковый тренд.

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