Environmental protection and sustainable development

INFLUENCE OF THE SIZE OF SILICON CARBIDE NANOPARTICLES ON THE ABRASIVE WEAR OF ELECTROLESS NICKEL COATINGS. PART 1

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Abstract. The present work represents the results of an investigation on wear and wear resistance of electroless nickel coatings with SiC nanoparticles of different sizes - 10, 45, 100, 150 and 700 nm under conditions of dry friction along the surface of firmly attached abrasive particles. The investigations carried out are split in two parts. In Part 1 are given the results concerning the influence of the nanoparticles of SiC with dimensions 10, 45 and 100 nm and in Part 2 will be given the results for nanoparticles of SiC with dimensions 150 and 700 nm. It has been established that the size of the SiC nanoparticles in combination with thermal treatment of the coatings exert substantial influence on the micro-hardness, on the character and the magnitude of linear wear, on the wear intensiveness and on the wear resistance of the coatings. The thermal treatment leads to increase in the micro-hardness of coatings without nanoparticles and coatings with nanoparticles. The highest wear resistance and micro-hardness is manifested by nickel coatings with the smallest size of the nanoparticles - 10 nm. Upon increasing the size of the SiC nanoparticles the wear resistance and micro-hardness decreased. It has been found out that in case of 10 nm nanoparticle size the kinetic curve of the wearing off process has linear character and the stage of co-operation of the coating is missing, which indicates high energy effectiveness of these coatings. Upon increasing the size of the SiC nanoparticles the kinetic curve acquires wave-like character with well expressed stage of gradual cooperation.

Keywords: tribology, abrasive wear, electroless nickel coatings, nanoparticles, silicon carbide.

AIMS AND BACKGROUND

The saving of energy and the protection of the environment are the top priorities in scientific and engineering-technological activities during the last decade. The tribological systems are of special importance for achieving rational utilisation of

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energy. It has been ascertained that more than 30% of the total energy produced in the world is consumed for overcoming the friction. The tribological studies contribute directly to energy saving by diminishing the friction and in this way they decrease the consumption of raw materials and reduce the demand for human resources because of the lower degree of wear and prolongation of the life cycle of mechanisms and machines.

The wearing off process is the basic reason for the damages in the machines and the equipment. More than 30% of all the failures in the main machine elements are direct consequence of wear, while more than 50% are the result of their tribological state – bad maintenance and control. The expenses as a consequence of abrasive wear of details, being some of the most often occurring types of wear, vary between 1 and 4% of the gross domestic product in developed countries 1-3.

One of the tendencies in tribology and in tribotechnologies to solve wear problems is to elaborate some new tribological coatings and modifications of the contact surfaces in tribo-systems^{4–25}.

Electroless plating is a method for deposition of coatings, in which one uses mainly chemical energy. Electroless plating is a process of chemical deposition, which can be defined as deposition of metal from aqueous solution of the metal salt by controllable chemical reduction, which is being catalysed by the metal or the alloy, which is being deosited8. Despite this fact, the process of formation of electrolytic coating has electrochemical mechanism, such as oxidation, as well as reduction, i.e. reactions, involving the transferring of electrons between the reactants. The oxidation of a given substance is characterised by loss of electrons (anodic process), while the reduction is characterised by increase in the number of electrons (cathodic action). The difference between electrolytic coating (chemical deposition) and galvanic coating (electrochemical deposition) consists in the manner, in which the electrons are supplied, needed for the reduction of the metal ions in the solution. The obtaining of galvanic coatings is based on decrease in the number of metal ions in the cathode, whereupon electrons are utilised, supplied by external source of direct current. The oxidation reaction is being accomplished on the anode of the same nature as the metal, which is being reduced on the cathode. In the case of electroless coating only one electrode (cathode) is being used without applying an external source of direct current. Instead of anode, the metal (the coating) is being supplied by the metal salt and the electrons are being liberated from a suitable chemical reducing agent, added to the solution. Since the coating is being deposited without any external source of electric current, no lines of electric current are being developed and because of this fact the thickness of the coating is uniform and homogeneous. As the system itself supplies the electrons, the process is called 'self-catalysing process'. The term 'electroless coating' is to some extent misleading. There are no external electrodes present, but there is electric current (charge transfer)^{26–39}.

The chemical composite coatings with nickel matrix have a series of advantages—high hardness, density and wear resistance. They copy the initial micro-relief of the surfaces, which enables their deposition on details having complicated shapes and thereafter they do not require consecutive mechanical processing. The studies during the recent years show that the electroless nickel coatings can successfully replace the galvanic chromium coatings, whose production has negative effect on the environment and on the human health. Although the ecological consequences of the nickel are not yet completely elucidated, it is obviously less problematic than chromium.

During the last 10 years unique results have been achieved to improve the tribological properties of chemical nickel coatings by adding to the nickel matrix nanosized particles of diamonds, carbides of silicon, tungsten, chromium, nitrides of boron and others. The presence of nanosized particles influences substantially the coefficient of friction and the intensity of the wearing off process. The interest in nanocomposite nickel coatings originates also from the circumstance, that in cases of some specific conditions of friction – loading, rate, composition of the surface layer and lubricating material there are occur processes of self-organisation in the tribo-systems, which lead to considerable energy effectiveness^{40–52}.

The surveying of the specialised literature shows that systematic tribological studies are missing regarding the influence of the sizes of nanoparticles of silicon carbide upon the characteristics of the wearing off process and upon the wear resistance of chemical nickel coatings.

The aim of the present work was to investigate the wear and wear resistance of electroless nickel coatings, containing nanoparticles of silicon carbide having different sizes under conditions of dry friction along the surface of firmly attached abrasive particles.

EXPERIMENTAL

Materials. The studies were carried out using samples of 8 types of electroless nickel coatings, which were prepared by the method EFTTOM-NICKEL, developed at the Technical University in Sofia^{36–39}.

The nickel (Ni) coatings comprise nanoparticles of SiC having sizes – 10, 45 and 100 nm; of one and the same concentration of nanoparticles varying from 5 to 7 vol.%. Half of the samples were subjected to thermal treatment at temperature 300 °C in the course of 6 h.

Table 1 presents the designation, description, thickness and micro-hardness of the tested coatings.

Table 1. Designation, thickness and microhardness of tested coatings

Sample	Designation	Description	Thickness (µm)	Micro- hardness HV _{0.5}
1	Ni	electroless Ni coating without nanoparticles and heat treatment	25.5	541
2	Ni^{HT}	electroless Ni coating without nanoparticles and with heat treatment	23.4	550
3	Ni–SiC10	electroless Ni coating with SiC nanoparticles of 10 nm size and without heat treatment	25.3	660
4	Ni–SiC10 ^{HT}	electroless Ni coating with SiC nanoparticles of 10 nm size and with heat treatment	24.0	895
5	Ni–SiC45	electroless Ni coating with SiC nanoparticles of 45 nm size and without heat treatment	23.6	610
6	Ni–SiC45 ^{HT}	electroless Ni coating with SiC nanoparticles of 45 nm size and with heat treatment	25.2	732
7	Ni-SiC100	electroless Ni coating with SiC nanoparticles of 100 nm size and without heat treatment	25.8	580
8	Ni–SiC100 ^{HT}	electroless Ni coating with SiC nanoparticles of 100 nm size and with heat treatment	24.8	681

In the designation of the samples the number after SiC shows the size of the nanoparticles, while the thermal treatment is denoted by the abbreviation HT.

All the coatings have been deposited upon the substrate of one and the same material – carbon steel St3kp (GOST 380-94) having chemical composition, shown in Table 2.

Table 2. Chemical composition (wt. %) of the coated material (substrate)

Element	С	Si	Mn	Ni	P	S	Cr	Fe
Percentage	0.40	0.20	0.55	0.30	0.45	0.045	0.30	balance
Microhardness				235	$HV_{0.5}$			

The samples represent disks of diameter 100 mm and thickness of 2.5 mm with identical roughness, which has been measured by mechanical profile meter TESA Rugosurf 10-10G. The average roughness of the initial coatings, measured in two perpendicular directions, is $R_{\rm a} = 0.089 \pm 0.05 \ \mu {\rm m}$.

The thickness of the coatings has been measured by the device Pocket Leptoskop 2021 Fe, whereupon it is accepted to be the mean arithmetic value out of 8 measurements. The microhardness (HV $_{0.5}$) of the coatings has been measured by means of microhardness meter device Vickers under loading of 500 g.

Figure 1 represents the microstructure of composite nickel coating containing nanoparticles SiC of size 10 nm with and without thermal treatment. The microstructure analysis showed that the Ni coatings with nanoparticles SiC without

thermal treatment have amorphous structure (Fig. 1 – left side), while the coatings after thermal treatment (Fig. 1 -right side) have crystalline structure. It is assumed that the thermal treatment leads to the appearance of stable crystalline structures, consisting of small crystallites, which improve the mechanical properties^{9,11,16}. The latter fact is in correspondence with the results, obtained by the authors with respect to microhardness of the studied coatings (Table 1).

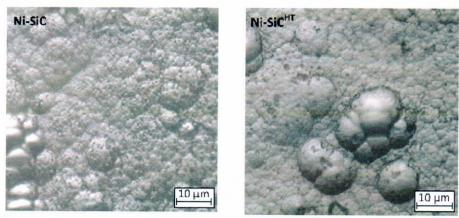


Fig. 1. Microstructure of the surface of coating Ni–SiC without thermal treatment (left) and after thermal treatment (right)

Device and methodology. Abrasive wear tests were carried out on Taber Abraser (Fig. 2) under modified standard test conditions (only one abrasive roller was used), in the ambient air at room temperature. The Taber Abraser generates a combination of sliding and rolling motion and it is primarily used for tests under mild abrasion conditions. A disc sample (1) with coating (2) is fixed on the horizontal turntable platform, driven at constant rotational speed (n) of 60 rpm by the electric motor (3). Abrasive roller (4), a Taber abrading wheel Calibrase CS-10, is mounted on horizontal axis (5) and it provides through weights (6) the necessary normal load (F_n). Abrasive roller (wheel) is driven by the rotating test sample. The wheels produce abrasion marks that form a pattern of crossed arcs over a circular ring. The width of the worn area (circular ring) is 12.7 mm, with the inner radius of 31.75 mm and outer radius of 44.45 mm.

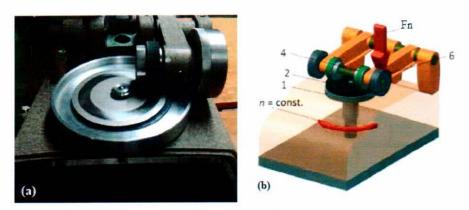


Fig. 2. Taber Abraser testing: image -a, and 3D model -b

Therefore, the distance between the rotational axis of disc sample (1) and mass centre of the contact area (K) is 38.1 mm, and the worn area is approximately 30 cm². The sliding action between the coated disc sample and abrasive roller is due to the relative motion between them which is characterised by the roller slip. Thus, the average tangential (sliding) velocity of the coated disc sample is 0.239 m/s.

Normal load of 250 g (2.5 N) was constant for all tests and coatings. The sliding distance (S) is calculated from the following equation $S = 2\pi rN$, where r = 38.1 mm is the distance between the rotational axis of disc sample and mass centre of the contact area, and N is the number of abrasion cycles.

The methodology of the study consists in determining the linear wear h as the difference between the initial thickness h_0 of the coating and the thickness of the coating h_i after a definite number of cycles of friction N_i (friction path S) $h = h_0 - h_i$. The intensiveness of the wearing off process is calculated based on linear wear per unit of friction path, i.e. i = h/S in μ m/m. The wear resistance is represented by the reciprocal value of the wear intensiveness, i.e. I = S/h in m/ μ m.

RESULTS AND DISCUSSION

The obtained results about the characteristics of the wearing off process – linear wear, wear intensiveness and wear resistance for different number of cycles N (friction path) are represented respectively in Tables 3, 4 and 5.

Figures 3, 4, 5 and 6 represent graphically the plotted dependence of linear wear on the number of friction cycles for all the tested samples – nickel coatings without nanoparticles and those having dimensions 10, 45 and 100 nm nanoparticles of SiC in the two cases – without thermal treatment and after thermal treatment.

Table 3. Linear wear of tested coatings

Sample	Coating	Number of cycles (N)								
	designation	100	200	300	400	500	600	800	1000	
		Sliding distance (m)								
		23.9	47.8	71.8	95.7	119.6	143.6	191.5	239.4	
		Linear wear (µm)								
1	Ni	7.4	11.8	16.5	22.4	25.1	-	1 -1 1	_	
2	Ni ^{HT}	4.5	6.0	7.2	9.7	10.8	12.4	16.1	23.0	
3	Ni-SiC10	6.6	8.4	10.3	12.1	14.0	15.4	18.4	20.5	
4	Ni-SiC10HT	2.2	3.8	6.3	7.4	8.8	10.2	11.4	13.8	
5	Ni-SiC45	8.9	10.6	12.2	14.9	16.1	17.3	19.5	22.4	
6	Ni-SiC45HT	3.8	4.9	8.1	8.9	9.8	11.2	14.0	16.2	
7	Ni-SiC100	6.9	12.4	15.4	16.1	17.4	18.5	21.3	25.1	
8	Ni-SiC100HT	5.8	8.1	12.6	13.3	13.9	15.2	18.6	20.4	

Table 4. Wear rate of tested coatings

Sample	Coating	Number of cycles (N)								
	designation	100	200	300	400	500	600	800	1000	
		Sliding distance (m)								
		23.9	47.8	71.8	95.7	119.6	143.6	191.5	239.4	
				1	Vear rat	e (µm/m	1)			
1	Ni	0.31	0.25	0.23	0.23	0.21	_	-	_	
2	Ni ^{HT}	0.19	0.13	0.10	0.10	0.09	0.09	0.09	0.1	
3	Ni-SiC10	0.28	0.18	0.14	0.13	0.12	0.11	0.10	0.09	
4	Ni-SiC10HT	0.09	0.08	0.09	0.08	0.07	0.07	0.10	0.06	
5	Ni-SiC45	0.37	0.22	0.17	0.16	0.13	0.12	0.10	0.09	
6	Ni-SiC45HT	0.16	0.10	0.11	0.09	0.08	0.08	0.07	0.07	
7	Ni-SiC100	0.29	0.26	0.21	0.17	0.15	0.13	0.11	0.10	
8	Ni-SiC100HT	0.24	0.17	0.17	0.14	0.12	0.11	0.10	0.09	

Table 5. Wear resistance of tested coatings

Sample	Coating	Number of cycles (N)								
	designation	100	200	300	400	500	600	800	1000	
		Sliding distance (m)								
		23.9	47.8	71.8	95.7	119.6	143.6	191.5	239.4	
			Wear resistance (m/μm)							
1	Ni	3.2	4.0	4.3	4.3	4.8	-	-	_	
2	Ni^{HT}	5.3	7.7	10.0	10.0	11.1	11.1	11.1	10.0	
3	Ni-SiC10	3.6	5.6	7.1	7.7	8.3	9.1	10.0	9.1	
4	Ni-SiC10HT	11.1	12.5	11.1	12.5	14.3	14.3	10.0	16.7	
5	Ni-SiC45	2.7	4.5	5.9	6.3	7.7	8.3	10.0	11.1	
6	Ni-SiC45HT	6.3	10.0	9.1	11.1	12.5	12.5	14.3	14.3	
7	Ni-SiC100	3.4	3.8	4.8	5.9	6.7	7.7	9.1	10.0	
8	Ni-SiC100HT	4.2	5.9	5.9	7.1	8.3	9.1	10.0	11.1	

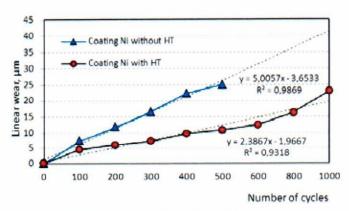


Fig. 3. Linear wear versus number of cycles for coatings without nanoparticles

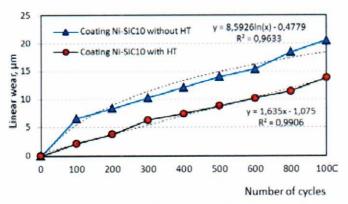


Fig. 4. Linear wear versus number of cycles for coatings with silicon carbide nanoparticles of 10 nm size

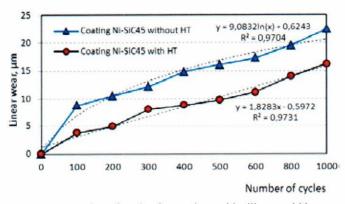


Fig. 5. Linear wear versus number of cycles for coatings with silicon carbide nanoparticles of 45 nm size

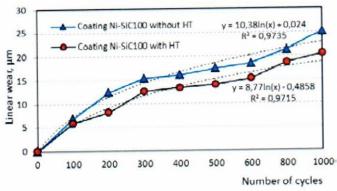


Fig.6. Linear wear versus number of cycles for coatings with silicon carbide nanoparticles of 100 nm size

It can be observed in the plotted graphs, that in the cases of coatings without nanoparticles and those with nanoparticles of small sizes – 10 and 45 nm, without thermal treatment and with thermal treatment the curve has linear character and the regime of co-working is missing. In the cases of the coatings having larger sizes of 100 nm, the dependence is non-linear and a period of co-working is observed. The longest duration is observed for the stage of co-working of coatings with 100 nm nanoparticle size. This is to be seen more clearly in the graphical dependences showing the changes in the wear intensiveness on the number of cycles, illustrated by Figs 7, 8, 9 and 10. What makes impression is the fact that in the cases of thermally treated coatings the wear intensiveness at smaller sizes of the nanoparticles 10 nm and 45 nm is constant (Figs 8 and 9). The presence of a stage of co-working and its duration in tribosystems is one of the criteria for judging their energy effectiveness.

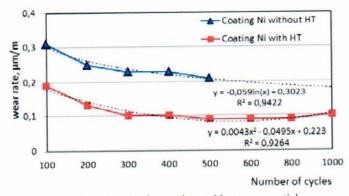


Fig. 7. Wear rate versus number of cycles for coatings without nanoparticles

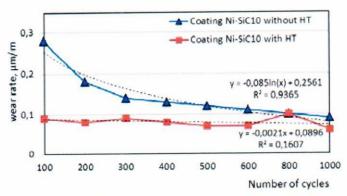


Fig. 8. Wear rate versus number of cycles for coatings with silicon carbide nanoparticles of 10 nm size

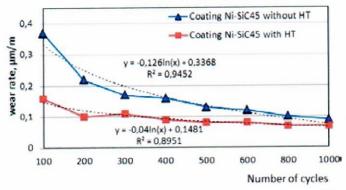


Fig. 9. Wear rate versus number of cycles for coatings with silicon carbide nanoparticles of 45 nm size

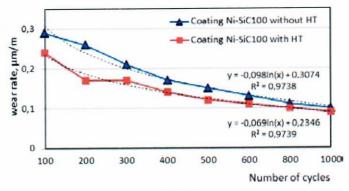


Fig. 10. Wear rate versus number of cycles for coatings with silicon carbide nanoparticles of 100 nm size

It becomes clear from the represented results that the thermal treatment and SiC nanoparticle size exert substantial influence on the characteristics of the wearing off process and on the wear resistance of the nickel coatings.

One can see from the data in Tables 3, 4 and 5 that the nickel coatings without thermal treatment and without nanoparticles exhaust their resource in case of friction path 500 cycles. The rest of the coatings under the same conditions of friction test have twice greater resource -1000 cycles.

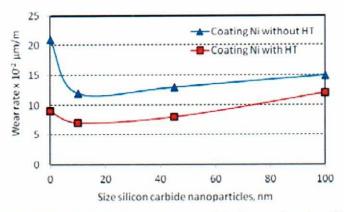


Fig. 11. Wear rate versus size of silicon carbide nanoparticles for tested coatings (500 cycles)

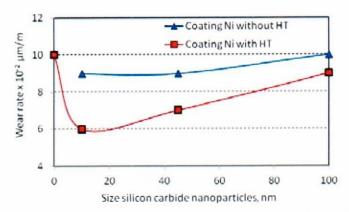


Fig. 12. Wear rate versus size of silicon carbide nanoparticles for tested coatings (1000 cycles)

The dependence of the wear intensiveness on the sizes of the nanoparticles of SiC has strongly expressed non-linear character showing minimum and maximum. Figures 11 and 12 illustrate the dependence of the wear intensiveness on the SiC particles sizes for coatings without and with thermal treatment in both cases of friction – after 500 and after 1000 cycles. The SiC nanoparticles lead to a decrease in the wear intensiveness for all kinds of tested coatings – with and without thermal treatment. The lowest wear intensiveness is manifested by the nickel coatings having nanoparticle size of 10 nm after thermal treatment. The coatings having nanoparticle size 45 nm also have lower wear intensiveness, compared to the rest of the samples, but higher with some 14% than that of the coatings with 10 nm

particle size (Table 4). It can be accepted that the best influence on the wear resistance of the coatings is displayed by SiC nanoparticles of sizes 10 nm and 45 nm.

CONCLUSIONS

The present research work reports comparative studies on wearing off process and wear resistance of electroless nickel coatings containing nanoparticles of SiC having sizes 10, 45 and 100 nm under the same conditions of dry friction along the surface of firmly attached abrasive particles. The obtained results show the ambiguity of effects and interconnected influence of the thermal treatment and the size of the nanoparticles of SiC upon the linear wear, the wear intensiveness and wear resistance.

The basic conclusions can be formulated as follows:

- − The thermal treatment leads to increase in the micro-hardness of the coatings without nanoparticles and coatings with nanoparticles. This fact correlates with the fine grain crystalline structure of electroless nickel coatings. The highest micro-hardness is shown by coating with thermal treatment having nanoparticle size of 10 nm − 895 HV, while the lowest micro-hardness is shown by coating with nanoparticles and without thermal treatment − 541 HV.
- The sizes of the nanoparticles SiC exert substantial influence on the wear intensiveness and respectively on the wear resistance of the nickel coatings. They lead to promotion of the wear resistance, whereupon this influence is more strongly expressed in the case of coatings without thermal treatment. It has been found out, that coatings having SiC nanoparticles of the smallest studied sizes 10 and 45 nm, and in combination with thermal treatment have the highest wear resistance.
- The sizes of the SiC nanoparticles exert substantial influence upon the character of the dependence of the wearing off process on the friction path length (the kinetic curve of the wearing off process) and the duration of the stage of coworking. In the cases of coatings of small sizes 10 and 45 nm the kinetic curve has linear character and the stage of co-working is missing.

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