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CAVITATION WEAR OF REINFORCED METAL SURFACES IN CORROSIVE ENVIRONMENTS

Summary. The paper considers the durability of polymeric coatings with PTFE, polypropylene and composite electrolytic coatings (CEC) on nickel matrix reinforced by silicon carbide particles of nano size (50 nm) and micro-size (80/100 microns). Cavitation test were carried out in neutral, acidic and alkaline media model.

Key words: polymeric, cavitation, CEP.

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КАВІТАЦІЙНА ЗНОСОСТІЙКІСТЬ ЗМІЦНЕНИХ МЕТАЛЕВИХ ПОВЕРХОНЬ У КОРОЗІЙНИХ СЕРЕДОВИЩАХ

Резюме. Розглянуто зносостійкість полімерних покриттів із фторопласту, поліпропілену та композиційних електролітичних покриттів (КЕП) з нікелевою матрицею, зміцненою частинками карбиду кремнію розмірами від нано- (50 нм) до мікрочастинок розміром (80/100 мкм). Випробування на кавітацію проведено в нейтральних, кислих і лужних модельних середовищах.

Ключові слова: полімери, кавітація, КЕП.

Statement of the problem. Cavitation-erosion wear resistance of metal alloys in corrosive environments is determined by mechanical and corrosive factors destruction. Corrosion, by itself, does not cause significant weight loss, but is a catalyst for fatigue fracture of metal surfaces at their micro shock loading in corrosive environments. Therefore, corrosion resistance, and in many cases complete chemical inertness against corrosive environments, caused the interest of researchers and practitioners in the use of plastic parts that will father contact with corrosive environments, particularly in terms of friction [1] and cavitation [2]. Despite of a number of significant advantages of plastics, their application is limited by lower, compared to metals, physical and mechanical properties and their high dependence on temperature. Combining the advantages of metal alloys and plastics can be achieved by coating the metal surfaces with polymer coatings [3, 4].

Analysis of many studies [5, 6, 7] shows that the combined electrochemical coating (CEC) based on nickel with inclusions of dispersed particles of carbides, nitrides, oxides have high wear resistance, corrosion resistance, increase the physical, mechanical and fatigue properties of metals and alloys. In general, CEC provide wear resistance, compared with clear plating by 2.5 ... 5 times [7]. When tested for durability CEP on nickel-based inclusions of carbides, borides, oxides show obvious advantage over 45 hardened steel, 45, 40X, 30ХГТ. The inclusion of carbides in a nickel matrix significantly improves wear resistance than the inclusion of oxides [1]. Prospects of inclusion, as a filler, nickel matrix silicon carbide has been indicated in many studies [5, 8]. The introduction of silicon carbide in a galvanic nickel coating significantly improves properties: microhardness increases by 1 ... 2.5 GPa, internal pressure decreases in 3 ... 8, corrosion resistance increased by 1.5 ... 2.5, and wear resistance 4 ... 5 times [6]. Surface of SiC are significantly higher bonding strength with the base material (steel 45) compared with the use of fillers as other carbides, respectively, SiC – 48.7; Cr₂O₃ –

44.0; Al_2O_3 – 26.5; Cr_7C_3 – 21.6 and TiC – 21.3MPa [9]. In addition, silicon carbide when compared with other carbides, has higher mechanical properties, higher corrosion resistance and melting point (2150 °C) as well as lower cost and produces industry in sufficient quantities in the form of powders of different fractions [6].

The methodology of the study. Polymer coatings were applied to steel samples normalized 45. On polished and defatted surface by electrostatic polymer layer deposited at $E = 1.0 \text{ kV / cm}$ for polypropylene and at $E = 2.0 \text{ kV / cm}$ for F4 PTFE (Teflon). Time for coating amounted to 30 min. In the work [10] it has been found that the optimum thickness of the coating on the metal in terms of anti-corrosion properties is 200...250 microns. Therefore, the thickness of coatings that were investigated was: for polypropylene at 200 mkm, and for PTFE – 250 mkm [10]. Choosing coating of polypropylene PP2 and PTFE F4 based on the results of previous studies [11].

Electrostatic method of polymer coatings is the most common because of the possibility of forming a uniform coating thickness which can be adjusted over a wide range. The bath (working chamber) with vibro-rotative method the boiling layer is created, which is under the category of corona electric field of high voltage. In the area of the corona is ionization of air to transfer electric charge of aerosol particles. When placed in boiling layer grounded cold pattern on its surface under the action of electric forces negatively charged particles are deposited onto polymer. Then cover is melted in a muffle furnace at $t = 200 \dots 210 \text{ }^\circ\text{C}$ for polypropylene PP2, and $t = 250 \dots 280 \text{ }^\circ\text{C}$ for PTFE F4 [10].

To implement CEP application was created to form CEP installation in a wide range of a process parameters of electrolysis both in horizontal and in the vertical cathode [12]. Setup lets you control the intensity of the near-electrode layer cathode and investigate its effect on the speed and quality of forming coatings.

As matrix for CEP nickel has been selected. Nickel has an affinity to the majority of particles that are used as the second phase - high mechanical properties, corrosion resistance. In addition, the rate of deposition of nickel electrolytes is the highest and most electrolytes are simple and stable during electrolysis [5, 6, 8]. To form CEP one typically uses sulfate or sulfate-chloride electrolyte nickel [6, 9], but chloride electrolytes speed up deposition of nickel, reaching 90...100 mm / h [31]. Therefore, the study uses nickel chloride electrolyte composition: 300 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ i 40 g/l H_3BO_3 з pH 3...4. In addition electrolyte was injected surfactant - sodium laurylsulfate of 0.01...0.02 g / l, which facilitates the inclusion of silicon carbide particles in a nickel matrix and stabilizes the chemical composition of the electrolyte during electrolysis [8].

As used filler dispersed amorphous boron powder with a particle size of about 1 micron and silicon carbide fractions: 50 nm - nanoparticles, M5, 28/20, 50/40, 100/80 mkm. Choosing the ability of boron due to its interaction with the nickel matrix at the next heat treated with the possibility of formation of solid solutions, eutectic, variance carbide. Accordingly, in the accepted designation: Ni + Ni+SiC_{nano} - nickel matrix filled with amorphous boron and SiC nanoparticles of 50 nm; Ni + SiC₅₀ - nickel matrix, amorphous boron and SiC particle size 50/40 microns, etc. As a result, were formed by coating consisted of only a nickel matrix Ni (needed for comparative data); Ni+SiC_{nano}; Ni+SiC₅; Ni+SiC₂₈; Ni+SiC₅₀; Ni+SiC₁₀₀. Deposition CEP on samples of steel 45 was performed at current density of 0.4 ... 1 kA/m², temperature $60 \pm 2 \text{ }^\circ\text{C}$ for 5 ... 6 hrs. and horizontal placement of the sample (cathode). Thickness of the coating is within 0.5...0.6 mm.

The heat treatment is carried out by coating annealing in vacuum at 1097 °C to form a solid Ni₃B borides and eutectic Ni-Ni₃B.

Electrochemical measurements were performed on a potentiostat ПІ5827М by the method described in [14]. Durability in micro shock loading in corrosive environments (CE)

was determined on the installation of the magnetostrictive vibrator (EOM). The study was conducted in hard water ($MgSO_4 \cdot 7H_2O$ - 0.0343 g and $CaCl_2$ - 0.51 g per 1 liter of distillate), 3% solution of sodium chloride, alkaline (CaO - 125g / l and 15% sucrose) and acid ($C_8H_8O_7$ - 5 g / l and Na_2HPO_4 - 10 g / l) environments.

Results and discussion. Research on cavitation-erosion wear resistance of polypropylene and surface on the basis shown (Fig.1,a), the coating based on polymer PP2 have slightly lower wear resistance than polypropylene in all studied environments. So, for 2h of durability testing the difference amounted to 1.35, 1.38 and 1.45 times, respectively, in neutral, acidic and alkaline environments. With the extension of the testing time difference in durability increases and in 3h micro shock load and amounts to 1.7, 1.68 and 1.51 times. Obviously, the reason for this difference is the velocity of sound waves in polypropylene and steel matrix, which causes the reflective waves intensify the process of destruction of the coating. In addition, the rate of destruction of polypropylene decreases and the surface on the basis, on the contrary, increases with continued time micro shock load. This is explained as a decrease in coating thickness and its structural changes that lead to a decrease in its elastic properties, and thus leads to increased energy reflecting sound waves (Fig. 1a, curves 1¹,2¹,3¹).

For coatings based on PTFE difference in wear resistance is negligible in comparison with samples of pure PTFE (Fig.1, b) and is a 3-hour cavitation from 6 to 11% in all studied environments. PTFE is completely neutral with respect to the studied media and the difference in wear resistance due to the physical parameters of the environment, causing shock and energy parameters reflecting waves at ultrasonic cavitation and hence the intensity of the fracture surfaces.

Depending on the type of environment research coverage on steel 45 normalized to cavitation-erosion resistance (ascending weight loss) are placed in a row: acidic, neutral and alkaline environment.

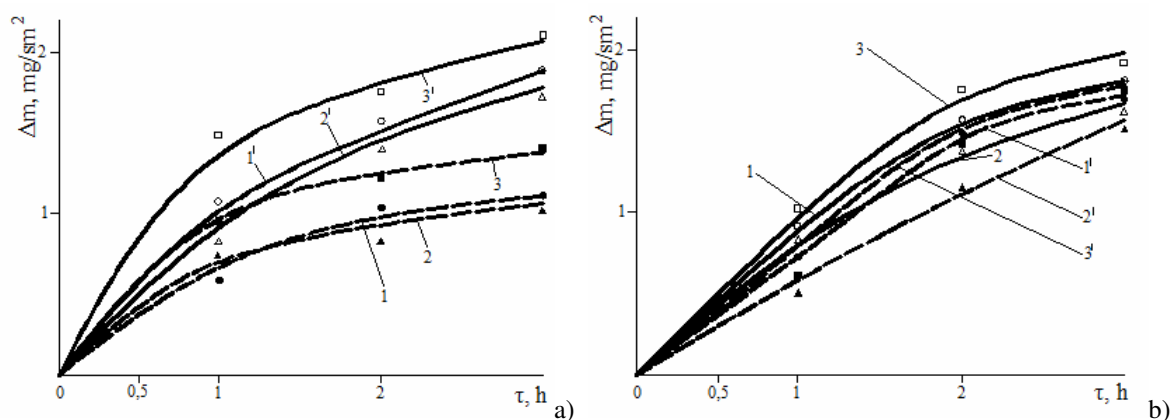


Figure 1. Cavitation-erosion resistance: a – polypropylene-PP2 1,2,3 and coverage based on polypropylene PP2 on steel 45 1¹,2¹,3¹; b - PTFE-F4 1,2,3 and surface on the basis 1¹,2¹,3¹, respectively, in neutral (1,1¹), acid (2,2¹) and alkaline environments (3,3¹)

Рисунок 1. Кавітаційно-ерозійна стійкість: а – поліпропілену ПП2 1,2,3 та покриття на основі поліпропілену ПП2 на сталі 45 1¹,2¹,3¹; б – фторопласту Ф4 1,2,3 та покриття на його основі 1¹,2¹,3¹ відповідно в нейтральному (1,1¹), кислому (2,2¹) та лужному середовищах (3,3¹)

Data analysis (Table 1) shows that the use of polymer coatings to enhance cavitation-erosion resistance of metallic alloys is a very effective way. Thus, in neutral medium coverage based on polypropylene and PTFE, PP2, F4 allow approximately 2 times increase in cavitation wear resistance of normalized steel 45.

Table 1

Type of environment	Material				
	Steel 45 normalized	Steel 45 + PP2	PP2	Steel 45 + F4	F4
Neutral	3,62	1,89	1,11	1,82	1,72
Acid	59,25*	1,78/1,23*	1,06/0,89*	1,67/1,34*	1,57/1,1*
Alkiline	1,71	2,08	1,38	1,98	1,78

* – weight loss for 2h cavitation

Especially effective is the use of polymer coatings in acidic environment, which increases the cavitation resistance more than by 40 times. Thus the use of PTFE for making cavitation resistant parts increases their durability more than by 50 times, and polypropylene - by 60 times.

It is known that the friction and cavitation in CAS, significantly accelerated the corrosion process. Because discrete contact of solid parts and discrete load surface micro volumes during cavitation get the impulse nature of the load, which determines the cyclical changes in stresses in the surface layer [15]. Thus, the friction and cavitation cyclic stress change indicates the nature of the fatigue fracture surfaces and the action of CAP, they must be seen as processes associated with adsorption and corrosion fatigue [14, 15]. The resulting decrease in adsorption limits of endurance - a consequence of the manifestation of the Rebinder effect [15].

The flow of adsorption processes is controlled by the size and nature of the change of electrode potentials. Adsorption, as a primary interaction act between the environment and the metal flows under control installed potential φ_{const} , and the localized adsorption of surfactants has a significant impact variable component of the total potential φ_{var} .

From the standpoint of physical and chemical mechanics of materials, adsorption reduces the surface energy, leading to a decrease of surface barriers that impede the movement of dislocations and facilitated their way to the surface. Due to heterogeneous electrochemical corrosion arising micro galvanic vapor facilitates active etching process in metal in places of dislocations, which under certain conditions can be the centers of origin of fatigue fracture [14, 15]. The above destruction mechanism is consistent with the structure of the investigated coatings, in which the frame of nickel matrix silicon includes carbide and amorphous boron (heterogeneous structure). It is therefore studied the kinetics of the change of potential component in neutral, acidic and alkaline environments (Fig. 2).

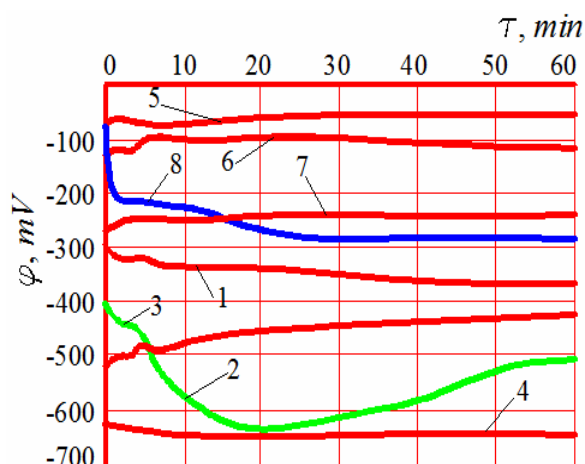


Figure 2. Kinetics of change in capacity of normalized steel 45: 1 – hard water, 2 – 3% – solution NaCl; 3 – alkiline, 4 – acid solution and steel covering 45 + Ni+SiC_{nano}: 5 hard water, 6 – 3% – solution NaCl; 7 – alkiline, 8 – acid solution

Рисунок 2. Кінетика зміни потенціалу сталі 45 нормалізованої: 1 – жорстка вода; 2 – 3%-ний розчин NaCl; 3 – лужний; 4 – кислий розчини і сталь 45+ покриття Ni+SiC_{nano}: 5 – жорстка вода; 6 – 3%-ний розчин NaCl; 7 – лужний; 8 – кислий розчини

The results of kinetics of potential changes in hard water first point to more noble potential of the coated samples (less negative potential values) compared with samples without coating. Characteristic is the fact that the potential of samples from CEP varies more smoothly than normalized, and its deviation from the set potential is much smaller. The later is the evidence of more evenly distributed over the surface of the thermodynamic potential and, more importantly, the inclusion of non-conducting particles in a matrix of SiC, that significantly reduces electromotive force elements micro galvanic coverage, confirming significantly lower values of potential negative samples from CEP. From the electrochemical point of view of CEP with inclusion of nano particles of SiC it has been shown the best results (Fig. 1, curve 5). Since the beginning of the testing the negative potential decreases and stabilizes quickly (3 min) reaching the set value of $\phi_{vst} = -76$ mV, which is the lowest value among all studied coatings. In addition, the composition of Ni+SiC₂₈ showed the least negative potential values (after composition Ni+SiC_{nano}) and tends to decrease with increase of its residence time in the environment. In [8] the highest durability with "direct" and "inverse" gradient structure coating with friction without lubrication has been also recorded for Ni+SiC₂₈.

In general, the value and uniformity of distribution of the thermodynamic potential surface, size and time to achieve specified potential ϕ_{vst} , changing nature of the curve potential-time in the tests conducted in hard water, the surface can be placed in series by the electrochemical degrading characteristics: Ni+SiC_{nano}; Ni+SiC₂₈; Ni+SiC₅₀; Ni+SiC₂₈+SiC₅₀; Ni+SiC₅; Ni; Ni+SiC₁₀₀; 45 normalized steel without coating.

Analysis of the kinetics of change of potential surfaces in 3% solution of sodium chloride shows an increase in negative potential values, but no significant change in the form of curves $\phi - \tau$. Thus, the CEP of Ni+SiC_{nano} also has the best electrochemical performance, but $\phi_{vst} \cong -117$ mV, which is significantly greater than $\phi_{vst} \cong -76$ mV in hard water (Fig. 2, curve 6). This can be explained by the significantly higher corrosion activity solution of NaCl. And the dissociated ions of chlorine and sodium significantly increase the conductivity of the solution, the activity and the electromotive force micro galvanic vapor. On top of that the same lane in a 3% solution of NaCl looks like the following sequence: Ni+SiC_{nano}; Ni+SiC₂₈; Ni+SiC₅; Ni+SiC₂₈+SiC₅₀; Ni+SiC₅₀; Ni; Ni+SiC₁₀₀; 45 normalized steel without coating. Similarly, the composition Ni+SiC₅; Ni+SiC₂₈ and Ni+SiC₂₈+SiC₅₀ are almost similar by curves of potential change in solutions of NaCl and hard water, and the potential values difference is also not significant [16].

Analysis of the kinetics of potential change in alkaline environment indicates the fastest time of its stabilization (Fig. 2, curve 7) and minor fluctuations in the value of the potential during the time trials. Thus, for the investigated coatings in alkaline environment and set the initial potentials are much less negative values compared to uncoated samples (Fig. 2, curves (3 and 7). Coatings filled with silicon carbide particles of different fractions are characterized by almost the same rates of potential ϕ_{vst} , which differ by the $\phi_{max} \cong -65$ mV, and the average deviation ϕ_{vst} from the initial potential is $\phi_{cp} \cong -35$ mV. Therefore a sequence of coatings in alkaline medium has the form: Ni; Ni+SiC₅₀; Ni+SiC_{напо}; Ni+SiC₅; Ni+SiC₂₈; Ni+SiC₁₀₀; Ni+SiC₂₈+SiC₅₀; steel 45 normalized without coating. The less favorable results shown by Ni+SiC₂₈+SiC₅₀ composition can apparently be explained by the fact that different-sized filler particles create different fields micro stress, causing an increase in the number micro galvanic vapor.

In acidic medium composition Ni+SiC_{nano} has one of the lowest values of the initial negative potential $\phi \cong -39$ mV. Unlike alkaline, the acidic considered CEP have a higher

negative potential and their negative potential constantly increases with time, which is a testament to their lack of corrosion resistance (Fig. 2, curve 8). In acidic environment the coverage for corrosion resistance are placed in sequence with degradinf SiC, ie, the smaller the particle size of the filler, the higher corrosion resistance of composition: Ni; Ni+SiC_{nano}; Ni+SiC₅; Ni+SiC₂₈; Ni+SiC₅₀; Ni+SiC₂₈+SiC₅₀; Ni+SiC₁₀₀. In addition, in acidic environment as opposed to alkaline and neutral, stabilizing potential during the time of testing does not occur, which is a testament to the relentless development of corrosion processes [17].

Study of the kinetics of change potential surfaces in neutral, alkaline and acidic media shows that an increase in corrosion activity environment installed capacity becomes more negative. Other applies to all tracks. Thus, for the composition Ni+SiC_{nano} the set potential of $\phi_{ocm} = -76, -117, -240$ and -300 mV, respectively, in hard water, in 3% solution of sodium chloride, alkaline and acidic environments.

Tests CEP in alkaline and acidic media have also shown that increased corrosion activity of the environment responds sensitively to the difference in volume microstress in the volume of the surface coverage caused by the difference of the size of the filler particles. With the increasing size of the filler particles increases the difference microstress and therefore the electromotive force of micro galvanic vapor, leading to an increase in negative surface potential. Kinetics of changes in potential of the surfaces in alkaline and neutral environments indicate promising applications considering compositions, in particular, to improve corrosion resistance in these environments. Indeed, installed capacity becomes a stable value in 3 ... 5 min from the beginning of the tests and in the future does not change its value, which is a testament to the electrochemical equilibrium in the system surface environment (Fig. 2, curves 5, 6, 7).

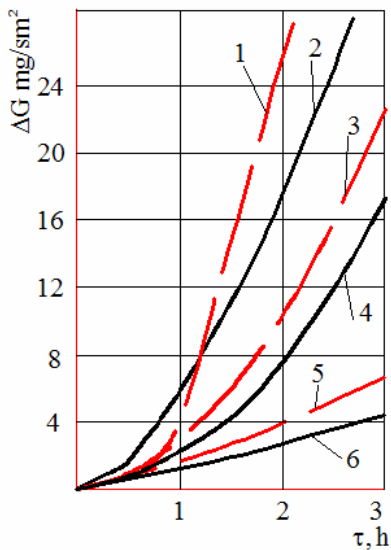


Figure 3. Kinetics wear under micro galvanic load: 1, 2, normalized steel 45, respectively, in 3% solution of NaCl and hard water 3, 4 - CEP Ni+SiC_{nano} in a 3% solution of NaCl and hard water, 5, 6 - CEP Ni+SiC_{nano} after annealing in vacuum in 3% solution of NaCl and hard water

Рисунок 3. Кінетика зношування при мікроударному навантаженні: 1, 2 – сталь 45 нормалізована відповідно в 3%-му розчині NaCl і жорсткій воді; 3, 4 – КЕП Ni+SiC_{нано} в 3%-му розчині NaCl і жорсткій воді; 5, 6 – КЕП Ni+SiC_{нано} після відпалу у вакуумі в 3%-му розчині NaCl і жорсткій воді

Testing for durability micro galvanic load in hard water and 3% solution of NaCl showed that KEП of Ni+SiC_{nano} protective coatings are effective only at the beginning of the test (within 1 h of cavitation), and then begins the destruction by its cover chipping (Fig. 3, curves 3 and 4). Other evidence of the lack of grip of nickel matrix material base, and various acoustic properties of the coating and the base cause lead coating from the base reflecting acoustic waves. Fractographic surface analysis also points to the possibility of stratification of coating by reflection of acoustic waves from particles of silicon carbide size of 50 microns and larger. After heat treatment in vacuum coating wear resistance increases significantly due to the formation and removal micro stress eutectic Ni+Ni₃B and hard borides Ni₃B (Fig. 3,

curves 5 and 6). Over 2 hours of cavitation weight loss are reduced in 1.86 ... 2.16 times compared to unstable models. On the property annealed coatings indicated by the fact that they are annealed in a muffle furnace at $t = 400^{\circ}\text{C}$ for 1 h increases the cavitation wear tracks Ni+SiC_{nano} 20 ... 30% in hard water and 3% solution of NaCl, respectively. This, along with the removal of micro stress around SiC particles improves their merging by nickel, increases the homogeneity of the structure and physical and mechanical properties.

Conclusions. Coatings based on polypropylene and PTFE somewhat inferior in terms of cavitation-erosion resistance of polypropylene and PTFE, but is effectively protected from damage of metal surfaces in neutral, acidic and alkaline environments.

Tested coverage induce 2 times increase in cavitation-erosion resistance of metal surfaces in neutral and more than by 40 times in acidic environments.

Most effective for use in alkaline environments is cavitation resistant details of polypropylene and at high mechanical loads of PTFE.

Composite fillings electrolytic coating of nickel matrix inclusions of particles of amorphous boron and silicon carbide various factions improve electrochemical parameters of the base of structural carbon steels (reduced stabilization time capacity, its negative value, amplitude) in all environments. The most effective is the composition of Ni+SiC_{nano} that much "ennobles" the value of building coverage and evens out the surface thermodynamic potential.

Considered composition CEP improve electrochemical parameters of the base the better, the higher corrosion activity environment. Especially promising is the use of these coatings in their contact with neutral and alkaline environments.

Durability in micro shock load composition Ni+SiC_{nano} in neutral and alkaline environments has increased by 1.32...1.45 times without subsequent heat treatment and by 1.86...2.16 after annealing in vacuum at 1097°C for 4 h and subsequent cooling.

Висновки. Покриття на основі поліпропілену та фторопласту дещо поступаються по кавітаційно-ерозійній стійкості поліпропілену та фторопласту, але є ефективним захистом металевих поверхонь від руйнування в нейтральних, кислих та лужних середовищах.

Досліджені покриття в 2 рази збільшують кавітаційно-ерозійну стійкість металевих поверхонь в нейтральних і більш як в 40 разів в кислих середовищах.

Найбільш ефективним для експлуатації в лужних середовищах є кавітаційностійкі деталі із поліпропілену, а при великих механічних навантаженнях із фторопласту.

Композиційні електролітичні покриття з наповнювачами нікелевої матриці включеннями частинок аморфного бору та карбиду кремнію різних фракцій покращують електрохімічні параметри поверхні основи із конструкційних вуглецевих сталей (зменшується час стабілізації потенціалу, його від'ємне значення, амплітуда коливань) у всіх середовищах. При цьому найбільш ефективною є композиція Ni+SiC_{nano}, яка значно «облагороджує» величину потенціалу покриття та вирівнює термодинамічний потенціал поверхні.

Розглянуті композиції КЕПів поліпшують електрохімічні параметри основи тим ефективніше, чим вища корозійна активність середовища. Особливо перспективним є застосування цих покриттів при їх контакті з нейтральними і лужними середовищами.

Зносостійкість при мікроударному навантаженні композиції Ni+SiC_{nano} у нейтральних і лужних середовищах підвищилася в 1,32...1,45 разів без наступної термообробки і в 1,86...2,16 після відпалу у вакуумі при температурі 1097°C протягом 4 год та подальшим охолодженням з камерою

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