Wear resistance of complex electrolytic coatings in electrolyte environments

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Abstract

The technology of formation of wear-resistant composite electrolytic coatings (CEP) based on nickel-based is presented. CEP. These coatings contained a filler consisting of powders of silicon carbide of various fractions and amorphous boron with a particle size of about 1 μm for further heat treatment. The obtained coatings were tested for their cavitation and erosion resistance in electrolyte media.

Key words: compositional electrochemical coating (CEP), cavitation, heat treatment, corrosion-resistant medium.

Introduction

In the general problem of increasing the reliability and durability of the machinery and equipment of the light, chemical and food industries, it is important to increase the reliability and durability of the parts subject to cavitation-erosion wear in corrosive environments. Thus, for operation in conditions of high specific pressures, loads, temperatures, vibrations, and circular and linear speeds, etc. parts are required, the working surfaces of which must have a whole set of physical and mechanical properties. For this purpose, technologies, methods and methods of surface hardening of work surfaces of parts are developed, which allow to use relatively cheap low carbon alloy steels with properties that are comparable to the properties of high alloy steels and special purpose alloys. One such surface hardening method is the development of heterogeneous composite electrolytic coating (CEP) technologies.

The use of these coatings to increase cavitation and erosion resistance in aggressive environments is limited due to insufficiently studied mechanisms of their formation, physical, mechanical and operational characteristics, and especially because there are no clearly stated requirements for cavitation and wear-resistant CEP requirements and methods of implementation.

Literary data analysis and problem statement

The analysis of works [1 - 6] shows that combined electrochemical coatings (CEP) based on Nickel with the inclusion of dispersed particles have high wear resistance, corrosion resistance, increase the physical-mechanical and fatigue characteristics of metals and alloys. In general, CEPs provide increased wear resistance, compared to pure galvanic coatings 2, 5 … 5 times [4]. Comparative tests for wear resistance indicate the advantage of nickel-based QES with the inclusion of carbides, borides, oxides in comparison with hardened steels 45, 40X. The inclusion of carbides in the nickel matrix significantly increases the wear resistance than the inclusion of oxides [2].

In particular, the analysis of nickel-based CEP [2, 7 - 12] shows the wide technological possibilities of changing their composition and properties, but they have lower durability compared to chrome coatings, low adhesion to the substrate, porosity. These disadvantages are sought to be eliminated by heat treatment of coatings in order to improve their physical and mechanical characteristics, wear resistance, corrosion resistance, etc. Thus, the authors of [13] state that the maximum adhesion strength of Ni-SIC coatings with aluminum alloys is achieved after annealing at a temperature of 200 °C for 2 h, but research [8, 10, 14] show a decrease in annealing at annealing in the temperature range of 200 … 700 °C. The microhardness of coatings with the inclusion of oxides and carbides decreased from 4.8 … 3.2 GPa to 3.2 … 2.0 GPa. The annealing effect on the cavitation wear resistance of Ni-SIC coatings was also not found.
Analysis of literature [2, 8, 10] shows that heat treatment of CEP can be effective only when introduced into the coating composition during its formation of substances or compounds, which in the subsequent heat treatment change the structure, phase composition of the coating. Thus, when introduced into the coating of amorphous boron in the Ni-B system at a temperature of 1060 ... 1080 °C eutectic is formed. Studies have also shown that annealing of the QES of the Ni-Cr7C3-B system at a temperature of 200 °C with a duration of 1 ... 2 h is sufficient to start the formation of borides and to obtain boride composite coatings [15]. Annealing of Ni - Cr and Fe - Cr compositions results in the formation of a stainless steel type coating [8]. In addition, thermal treatment of CEP is performed by laser, high-frequency currents that provide high rates of heating and cooling, locality and discretion of processing [10, 16], but these methods are expensive and not well-researched.

The use of these coatings to increase cavitation and erosion resistance in aggressive environments is very limited due to the lack of studied mechanisms of their formation, physical, mechanical and operational characteristics, and especially because there are no clearly stated requirements for cavitation and wear resistant CEP, ways to implement these CEP requirements. There are no data on the ratio of the proportion of solid inclusions and the metal base, composition, shape and geometric size of the particles of the strengthening phases, their bulk content in the matrix, which significantly limits the possibilities of purposeful control of the process of formation of a complex of anti-wear properties of CEP. Therefore, the urgent task is to research and systematize the cavitation-erosion, corrosion and electrochemical characteristics of the CEP, the features of the formation of their structure, the effect of heat treatment on the wear resistance of the coatings and the possibilities of purposeful change of the characteristics of the coating, depending on the conditions of external microwave loading, corrosion activity of the environment. Therefore, the urgent task is to research and systematize the cavitation-erosion, corrosion and electrochemical characteristics of the CEP, the features of the formation of their structure, the effect of heat treatment on the wear resistance of the coatings and the possibilities of purposeful change of the characteristics of the coating, depending on the conditions of external microwave loading, corrosion activity of the environment.

Aims and objectives of research

The purpose of this work is to study and systematize the cavitation-erosion characteristics of CEP in electrolyte media, the features of their structure formation, the effect of heat treatment on the wear resistance of coatings and the possibilities of purposeful change of the coating characteristics depending on the conditions of external microwave loading, corrosion activity of the environment.

Research results

To achieve this goal, an installation was created for the formation of CEP in a wide range of technological parameters of electrolysis on both horizontal and vertical cathodes [18].

Nickel is chosen as the matrix for CEP. Nickel has an affinity for most of the particles that you use as a second phase, high mechanical properties, corrosion resistance. For the formation of CEP used chloride electrolytes, which provide the deposition rate of Nickel 90 ... 100 μm / h, simple and stable in the electrolysis process [2, 3, 11, 18]. The work used the nickel chloride electrolyte of the following composition: 300 g/l NiCl₂; 6H₂O i 40 g/l H₂BO₃; 3 pH 3 ... 4, and additionally introduced surfactants - sodium laurisulfate in an amount 0,01 ... 0,02 g/l, which facilitates the incorporation of SiC particles into the nickel matrix and stabilizes the chemical composition of the electrolyte in the electrolysis process [11]. As the filler used dispersed powders of silicon carbide fractions: about 50 nm - nanoparticles; M5; 28/20; 50/40 μm.

Accordingly, the designation was adopted: Ni-SiCnano - a nickel matrix with a nanowire filler, SiC size 50 nm, etc. As a result, Ni-SiCnano coatings were formed; Ni-SiC5; Ni-SiC28. The deposition of QES on samples of steel 45 was carried out at a current density of 0.4 ... 1 kA / m², a temperature of 60 ± 2 °C for 5 ... 6 h, and horizontal placement of the sample (cathode). The thickness of the coating was within 0.5 ... 0.6 mm. Wear resistance at micro shock impact in corrosive environments (CAS) was determined on the installation with a magnetostrictive vibrator (MV). The studies were carried out in hard water (MgSO4·7H₂O – 0,0343 g and CaCl₂ – 0,51 g per liter of distillate), and 3 % sodium chloride solution.

Analysis of Ni-SiC state diagrams shows that silicon carbide does not interact with nickel and melts only at 2150 °C. Thus, only the recrystallization of the matrix and partial reduction of residual stresses occur in the thermal treatment of CEP of the Ni-SiC composition. At the same time, eutectic with a mass content of 4.2 % is formed in the Ni-B system [20]. The eutectic formation temperature is 1060 ... 1080 °C.

Vacuum diffusion annealing of CEP Ni-B at temperatures not exceeding the eutectic formation temperature results in a uniformly distributed volume of Ni3B boride matrix. Thus, the exposure for 1 ... 2 h at a temperature of 200 °C is already sufficient to start the formation of borides and obtain boride composite coatings [21]. Heating the coatings to the formation temperature of the eutectic allows to obtain pre-eutectic structure. The Ni-Ni,B eutectic forms a kind of rigid framework with a soft component located in the intervals [21, 22].

Therefore, to improve the efficiency of heat treatment in order to improve the physico-mechanical characteristics of the CEP, it is necessary to co-exist with particles of silicon carbide and particles interacting with a nickel matrix, for example, particles of amorphous boron, which at a temperature of 1060 ... 1080 °C form
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with Nickel Ni3B borides and Ni-Ni3B eutectic with high hardness, cavitation and erosion resistance [23, 24], corrosion resistance [25, 26].

By introducing boron particles into the nickel matrix, its microhardness slightly increases to $H_\mu = 3.2 \ldots 3.6$ GPa. CEP, in which besides boron particles are also present silicon carbide particles, have higher microhardness $H_\mu =3.8\ldots4.6$ GPa, which is explained by the larger lattice distortions, the increase in the density of dislocations with the simultaneous dispersion of nickel hardening by boron particles, which block the movement of dislocations in the coating.

Thermal annealing in a muffle furnace at 400 °C for 1 … 2 h leads to an increase in the cavitation-erosion resistance of the Ni-SiC composition by about 20 % in hard water and about 30 % in a 3 % NaCl solution [118] due to the decrease and alignment of internal stresses in the coating, the decrease in heterogeneity of the structure (Fig. 1). The annealing temperature is selected for the reason that irreversible transformations and eutectic formations take place in the temperature range 120 … 220; 300 … 350 and 370 … 450 °C [117].

![Graph showing wear kinetics at micro-shock load](image)

**Fig. 1. Wear kinetics at micro-shock load:**
1, 2 – steel 45 normalized, respectively, in 3 % NaCl solution and hard water;
3, 4 – CEP Ni-SiCan in 3 % NaCl solution and hard water;
5, 6 – CEP Ni-SiC found after annealing in vacuum in 3 % NaCl solution and hard water

Vacuum annealing with the melting of the surface of the coating was performed on the installation of OKB 8086 at temperatures of 1085 ... 1090 °C. After holding in the oven, the samples were cooled with the oven.

In Fig. 2, and shows the microstructure of the coating Ni-SiC28-B without heat treatment, in which the large time-plaster is the inclusion of SiC28, and small - particles of boron. After heat treatment, the microstructure forms a carcass consisting of eutectic Ni-Ni3B and Ni3B borides (Fig. 2, b) with hardness $H_\mu =6.6\ldots7.4$ GPa.

![Microstructure images](image)

**Fig. 2. The microstructure of the coating Ni-SiC28-B:**
\[ a \] – initial state;
\[ b \] – after vacuum annealing
The X-ray diffraction analysis showed the presence of 67.63 nickel in the CEP and 32.37 mc of the Ni3B boride. % respectively. The cavitation-erosion tests of QES Ni-SiC28-B after vacuum annealing in hard water showed (Fig. 3) that the wear resistance increased by 2 hours (curve 3), compared to QES without vacuum annealing (curve 1) 2 times. Therefore, vacuum annealing at the temperature of eutectic formation allows to obtain dense smooth coatings with high cavitation and erosion resistance.

![Fig. 3. Weight loss in cavitation of CEP Ni-SiC28-B in hard water:](image)
- 1 – without heat treatment;
- 2 – after heat treatment;
- 3 – after melting in vacuum

The widespread use of nickel-based CEP is explained by the fact that it is easily coprecipitated with most dispersed particles of different nature - carbides, borides, nitrides, oxides, metals and non-metals [24 - 28, 30]. CEP with nickel base and dispersed particles of different nature are used for under-increasing corrosion resistance, decorative and protective properties, wear resistance during friction and cavitation, heat resistance, etc. To increase the heat resistance of CEP based on Nickel as a filler used time-slings SiC, SiO2, Al2O3, TiO2, TnO2, ZnO and others. [29]. The studies conducted above have shown that corrosion resistance, as well as studies of kinetics of change of potential and analysis of polarization curves can characterize in the first approximation the cavitation-erosion resistance of CEP in the medium [18-21]. However, there is a hypothesis about the thermodynamic theory of cavitation erosion [30], which is closely related to the hypothesis of instantaneous chemical reactions [32]. According to these hypotheses, when the cavitation bubbles collide, outbreaks of temperatures of 3000 ° C and above develop [11], which lead to the development of instantaneous chemical reactions, which significantly reduce the physico-mechanical and corrosion characteristics of the surfaces. Our studies have confirmed the significant effect of ambient temperature on the cavitation-erosion resistance of metals [6] and polymers [23], which is caused by a significant increase in the surface temperature, which is subject to the cavitation action of the medium.

To simultaneously increase the complex of physical, mechanical and electrochemical properties of surfaces, while increasing their cavitation and erosion resistance, CEP was developed with the inclusion of eutectic alloy and subsequent heat treatment (patent № 49210 of Ukraine dated 26.04.2010).

The composition of the electrolyte is additionally introduced by the inclusion of eutectic alloy spherical shape, with a diameter of 20-100, which include,% by weight: boron - 6.1 ... 8.2; chromium - 20.4 ... 27.1; Nickel - 10.1... 20.2; titanium - 12.7 ... 16.4; iron - the rest, at the following ratio of components of the electrolyte, g / l: Nickel chloride (or iron or cobalt) - 400; boric acid - 40; amorphous boron - 10 ... 40; eutectic alloy (powder) - 10 ... 35 [124].

Introduction to the metal matrix CEP simultaneously amorphous boron and eutectic alloy favorably distinguishes the composition for obtaining CEP from the known fact that the presence of its inclusions at the same time eutectic alloy and amorphous boron allows to carry out, by analogy with carbon in iron, heat treatment with CE with the formation in the matrix of the CEP dispersed segregations of borides Ni3B, Fe3B, CO2B and others. The composition of the eutectic filler composition is selected such that nickel and partially chromium dissolve in the iron within the solid solution. This forms a solid solution on the basis γ-Fe, alloyed with chromium and nickel at concentrations that give it maximum heat resistance under high temperature oxidation in air. In addition, titanium and chromium particles form chromium and titanium borides, which impart high alloy durability at elevated temperatures in corrosive environments. To obtain the CEP from the electrolyte, the electroplating process of electroplating metal and the filler powders contained in the electrolyte was performed on pre-degreased and etched steel samples from nickel chloride electrolyte.

The process was carried out at temperatures from 40 to 60 °C, pH from 3 ... 4, current density from 5 to 15 A / dm² with constant stirring of the electrolyte with a pulse stirrer. The content in the electrolyte of boron particles was set in the range from 10 to 80 kg / m³, and the eutectic alloy from 10 to 35 kg/m³. The obtained coatings according to the chemical analysis contained from 0.5 to 6.0 wt.% Boron and from 10 to 44.2 wt.% Eutectic alloy, and after annealing in the temperature range from 200 to 1050 for 0.5 to 5 h had a structure...
uniformly distributed in the metal matrix from a solid boron solution of inclusions of the corresponding borides Ni3B, Co2B, Fe2B and inclusions of the eutectic alloy.

The lowest onset temperature of Ni3B boride formation is fixed at 200, and an annealing temperature higher than 1050 leads to eutectic melting of the coating. Electrolyte input less than 10 kg/m³ boron does not provide the required number of inclusions for the occurrence of boride phases in the CEP.

The introduction of eutectic alloy particles into the CEP increases its heat resistance, especially the coating on the basic iron (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>The basis of QES</th>
<th>Inclusion of eutectic alloy, mass %</th>
<th>Weight change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td>Fe</td>
</tr>
<tr>
<td>prototype</td>
<td>Ni або Fe</td>
<td>1,5</td>
<td>7,1</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>10,2</td>
<td>1,4</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>16,0</td>
<td>1,0</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>25,2</td>
<td>0,7</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>29,0</td>
<td>0,6</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>33,1</td>
<td>0,6</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>40,2</td>
<td>0,9</td>
</tr>
</tbody>
</table>

The high-temperature oxidation of the coatings was investigated on a thermomassometer TM-50 installation in air at 600 temperatures with the sample holding for 6 hours.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Measured.</th>
<th>Prototype samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1     2     3     4     5     6</td>
</tr>
<tr>
<td>The composition of the electrolyte</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>kg/m³</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Boric acid</td>
<td>kg/m³</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>Boron amorphous</td>
<td>kg/m³</td>
<td>10-30</td>
<td>12</td>
</tr>
<tr>
<td>Eutectic alloy</td>
<td>kg/m³</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Electrolysis mode</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathodic current density</td>
<td>kA / m²</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Electrolysis time</td>
<td>h</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Annealing modes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>1000-1100</td>
<td>150</td>
</tr>
<tr>
<td>Duration</td>
<td>min</td>
<td>180</td>
<td>420</td>
</tr>
<tr>
<td>Mass fraction of components in CEP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron amorphous</td>
<td>% mas.</td>
<td>3,5</td>
<td>0,25</td>
</tr>
<tr>
<td>Filler</td>
<td>% mas.</td>
<td>-</td>
<td>10,2</td>
</tr>
<tr>
<td>Nickel (iron, cobalt)</td>
<td>% mas.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characterization of the microstructure of the substrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eutectic + nickel boron</td>
<td>Mechanical mixture of nickel boron</td>
</tr>
<tr>
<td>Hard water</td>
<td>mg / cm²</td>
<td>8,7</td>
<td>9,0</td>
</tr>
<tr>
<td>3% NaCl</td>
<td></td>
<td>64,1</td>
<td>60,8</td>
</tr>
<tr>
<td>Acidic environment</td>
<td></td>
<td>24,2</td>
<td>25,4</td>
</tr>
<tr>
<td>Alkaline environment</td>
<td></td>
<td>29,6</td>
<td>31,8</td>
</tr>
</tbody>
</table>
From the data table. 5.1 shows that the maximum heat resistance of QES, in whose content of eutectic filler is 25 - 33 wt.% (coverage 3-5). QES of such an alloy are formed at the declared content of eutectic particles in the electrolyte; 10 - 35 g/l. Reducing the content of the filler leads to a decrease in the heat resistance of the coating due to the formation of porous oxide films in nickel or iron base. Exceeding them also reduces heat resistance, but due to the cracking of the coating and its increased porosity, which intensifies the oxidation processes.

Tests for cavitation and erosion resistance were carried out on the installation with the Ministry of Internal Affairs according to the method described in section 2. The results of the wear resistance of the coated specimens on the developed composition of the eutectic filler alloy under different modes and conditions of formation of CEP in hard water and in 3% sodium chloride solution and alkaline model environments are given in table 2. The analysis of the obtained results showed (Table 2) that the cavitation-erosion resistance of the formed (Table 1) and heat-treated by the optimal mode of QES increases in comparison with the nickel matrix in 2.4; 2.2; 2.4 and 3.4 times in hard water; 3% solution of NaCl, acidic and alkaline model media were recovered.

The obvious advantages of the composition in comparison with the nickel matrix are the different reduction of the temperature of the heat treatment, which allows to change the microstructure of the CEP within a wider range. In addition, the cost-effectiveness of CEP based on the iron group is reduced by more than 2 times.

At a temperature of 600 °C (Table 1), the mass loss in the air is mainly due to the removal of the oxide films. The oxide film formed in the air must be of optimum thickness. From the table. 1 shows that samples 3-5 have 2 ... 2.5 times less mass loss during high-temperature oxidation, which apparently led to an increase in cavitation-erosion wear resistance of the CEP in the investigated media approximately within the range (2.2 ... 3, 4 times).

Main results and conclusions

1. The cavitation-erosion wear resistance of CEP formed by optimal modes of electrolysis, the content of filler particles in the electrolyte and in the nickel matrix, depending on their geometric dimensions in neutral, alkaline and acidic environments, was investigated.

2. Thermal annealing at 400 °C for 1 ... 2 h increases the cavitation wear resistance of CEP Ni + SiC by 20 % in hard water and by 30 % in NaCl solution, which is explained by the increase of microhardness and the alignment of internal stresses of the coating and the increase of corrosion resistance due to the decrease in corrosion resistance.

3. Vacuum annealing of CEP with particles of silicon carbide and boron at 1080 - 1090 °C allows to obtain dense and smooth coatings cavitation wear which increases on average more than 2 times due to the formation of a solid framework of eutectic Ni-Ni3B and Ni3B borides.

4. The developed composition of heat-resistant eutectic granules of a spherical filler with a diameter of 20 ... 100 μm with its content of 10... 100 g/l in the chloride electrolyte allows to increase the heat-bone by 2 ... 2.5 times and to 2.2 ... 3.4 times by cavitation - Erosion resistance of CEP in all media compared to the wear resistance of the Nickel matrix coating (Patent No. 49210 of Ukraine dated 26.04.2010).

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Білик Ю.М., Мартинюк А.В., Медведчук Н.К., Купець Б.І. Зносостійкість комплексних електролітичних покриттів в середовищах-електролітах.

У роботі подана технологія формування зносостійких композиційних електролітичних покриттів (КЕП) на нікелевій основі. КЕП містили наповнювач, що складався з порошків карбіду кремнію різних фракцій і аморфного бору з розміром частинок біля 1 мкм для можливості подальшої термообробки. Проведено випробування отриманих покриттів на їх кавітаційно-ерозійну зносостійкість в середовищах-електролітах.

Ключові слова: композиційні електролітичні покриття (КЕП), кавітація, термообробка, корозійно-активні середовища.