Investigation of the metal surfaces destruction due to electrochemical corrosion and cavitation, methods of protection with the use of polymer composite coatings based on CNT

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Abstract. The study is devoted to the dynamics of the appearance and development of defects at the nanoscale level for stainless steel and screw bronze of certain grades using electron, atomic force microscopy. The main mechanisms of destruction have been identified and a comparative analysis of the materials studied has been carried out. The results are presented on the possible protection of the material by applying a metal/polymer coating based on epoxy resin with different CNTs concentrations.

1. Introduction
One of the crucial problems in modern shipbuilding and ship repair is the increase of durability and the prolongation of the service life of a critical parts group (elements of screw-propellers, shafts, turbines). Cavitation and electrocorrosion are among the main causes of screws destruction of sea-going ships [1-2]. The stage of the appearance, dynamics and evolution of defects at the nanoscale is the least studied from the point of mechanism cavitation action view. Changing the time and regimes of the cavitation and electrocorrosion action on the samples, the authors observe the dynamics of the defects appearance and development. This allowed us to identify the main mechanisms of destruction and to carry out a comparative analysis of the materials studied to develop recommendations for their use in shipbuilding and ship repair, as well as to draw a conclusion about the functional options for protection.

2. Method
The essence of the new technique is that the samples of the metal alloys used for the production of screw-propellers are subjected to cavitation and electrocorrosion by a specially assembled stand (Fig. 1). As a source of cavitation effect, an ultrasonic magnetostrictive vibrating piezoelectric driver is used, placed in an electrolytic bath with a sample in water with an adjustable salt content. Varying the time of the main mechanisms destruction action – cavitation and electrochemical corrosion allowed in the laboratory to simulate the destruction of screw-propellers surface of the sea vessels. The state of the surface, the change in the relief and the roughness due to the appearance of various types defects of nanometer resolution were controlled by the methods of electron and scanning probe microscopy (ESM, SPM) according to the approach [3]. The combination of these methods of investigation made it possible to reveal temporal dynamics and mechanisms of destruction, as well as to conduct a comparative analysis of various alloys samples.
3. Cavitation and electro corrosive destruction of screw-propeller materials

On the basis of the above procedure, a study was made of the metal alloys samples (corrosion-resistant steel grade 08X18H10T (AISI 321), screw bronze BrA9Zh4N4) subjected to cavitation and electro corrosive hydrodynamic effects of varying duration. Figure 2 shows the surface roughness as a function of the ultrasound treatment time of steel and bronze samples measured by SPM microscopy.

The presented results allow dividing the effects of the cavitation action into two stages: surface smoothing for four hours (grinding effect) and subsequent development and evolution of defects. The destruction of steel is slow enough compared to a bronze sample. For a bronze specimen, noticeable changes in the relief and roughness occur only after 6 hours of cavitation action. Damage to the surface has local character. Only after 6 hours of ultrasound treatment the cavitation effect significantly changes the near-surface layer the appearance of deep cavities begins, after 12 hours of cavitation action, the average roughness increases one and a half times to values of the 50 nanometers order (Fig. 3). The study of cavitation fracture of steel samples revealed high anticavitational resistance, in relation to samples of screw bronze. At the initial stage, cavitation smooth the initial roughness, then further slightly increasing the average roughness to 40–50 nanometers for 15 hours of exposure (Fig. 4). The stages and character of steel destruction have distinctive from the bronze sample. The main contribution to the destruction of the surface layer is made by electrochemical corrosion. The authors conducted a study of the development defect dynamics through such destruction action. Salinity of water in the electrolytic bath is 3%, potential is 3V, the anode current is from the sample of 0.2 A. For a bronze sample, electrochemical corrosion primarily destroys the passivation layer on the surface, which is created by the presence of nickel in the alloy.

![Figure 1](image1.png)

**Figure 1.** Researching stand. 1 – metal sample, 2 – water (salinity 0÷30‰), 3 – boxing, 4 – dispersant tip, 5 – ultrasonic disperser.

![Figure 2](image2.png)

**Figure 2.** Dependence of the surface roughness on the time of ultrasound treatment for steel and bronze samples (red and blue colors, respectively).
Figure 3. ESM photo of the bronze samples after the cavitation action. Exposure time is 0, 6, 10 hours respectively.

Figure 4. ESM photo of the steel samples after cavitation action. Exposure time is 0, 5, 15 hours respectively.

Figure 5. ESM photo of the bronze samples after electrochemical corrosion. The exposure time is 10, 30, 60 minutes respectively.

For 30 minutes, the roughness increases twofold. During this time, a passivation layer with a thickness of the order of 50 nanometers completely disappears. Then, intercrystalline and intracrystalline corrosion develops, which leads to considerable surface degradation with an increase in the average roughness to values greater than 5 μm in a time of the order of 60 minutes (Fig. 5). With respect to electrochemical corrosion, steel samples are destroyed more intensively. At comparable values of the
anode current, the destruction of the passivating layer occurs two times faster. In this case, the grain structure is more clearly exposed and intercrystalline corrosion begins, leading to an increase in the average roughness above 5 μm in a time of the order of 30 minutes (Fig. 6).

Figure 6. ESM photo of the steel samples after electrochemical corrosion. The exposure time is 10, 30, 60 minutes, respectively.

Table 1 shows the mass loss values for two samples (steel, bronze) with two action regimes (electrocorrosion and electrocorrosion + cavitation). Note that for an hour of electrochemical corrosion, both samples experience an equal mass loss of 15%. However, the combined effect of electrocorrosion and cavitation leads to different results. For the bronze sample, the loss effect is enhanced, while for the steel sample, the loss effect is reduced. This effect is attributed to the competition between the intercrystal and the intracrystal of electrocorrosion in these alloys. Steel is dominated by fracture due to intercrystalline corrosion, which is slowed by cavitation flows. In bronze, intragrain corrosion prevails, which is accelerated by the washing out of the passivization layer due to the cavitation effect.

|                | Electrochemical corrosion | Electrochemical corrosion + cavitation |
|----------------|---------------------------|----------------------------------------|
| **Bronze**     | 15%                       | 23%                                    |
| **Steel**      | 15%                       | 7%                                     |

4. Development of a nanocomposite CNT coating for the protection of materials from destruction in hydrodynamic media

Currently, screw-steering columns are being developed in which the transfer of torque from the engine to the screw goes through the generator and electric motor system, while the screw is attached directly to the motor armature, so the screw is in the area of intensive alternating electromagnetic field induced by the windings of the electric motor. Therefore, for the development of coatings with carbon nanotube (CNT), it is necessary to study such materials for the electrophysical properties of such polymers depending on the CNT concentration. The study of concentration effects, the percolation threshold and the electrophysical properties of polymer composite materials is given in [4]. Based on the results of [4, 5] the authors propose to use as a anticorrosion coating a polymer composite material with the CNTs addition. Here the CNTs would perform the role of both the reinforcing element and the intermediate link in the metal/polymer system to increase adhesion with the surface.
Figure 7. Boundary layer of the metal/polymer sample after electrochemical exposure with a concentration of CNT in the polymer of 0, 1, 2%, respectively.

The results of corrosion damage study of the samples with coatings based on epoxy resin with different concentration of CNT are shown in Fig. 7. The samples were subjected to intensive electrochemical exposure in a salt bath after that the boundary of metal/polymer was investigated by the ESM method. Samples of a small (up to 1%) concentration of CNTs were found to be more resistant to the distraction. In a sample with a polymer without CNTs, large polymer fibers are torn off at the boundary, but it is more resistant to destruction than the sample with 2% of the CNT additive. In this case (beyond the percolation threshold), nanotubes obviously act as conductive defects that accelerate the destruction. We also note that the methods and regimes for applying such a coating, the exact concentration, the type of CNTs require further investigation and refinement.

5. Conclusions

We formulate main conclusions and results.

- A technique for studying the dynamics of defect evolution and development in the structure of screw-propeller metals due to cavitation and electrochemical corrosion action in a hydrodynamic medium are developed.
- Investigations of the defects evolution were carried out on the example of two materials widely used in the shipbuilding industry: corrosion-resistant steel grade 08X18H10T (AISI 321), screw bronze BrA9Zh4N4. The results of SPM and ESM of the defect dynamics and development are presented. Characteristic features of defect formation are revealed.
- The research of metal protection new methods by coating them with a composite polymer material with the addition of CNTs was proposed and started.

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