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Development of nanostructured anti-fouling coatings for hydro plant facilities

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Abstract

The biofouling is a serious technical issue in hydropower facilities operating in a freshwater environment. The presented novel technology of antifouling coating integrates two functionalities of deposited material - biocidal features of copper and superhydrophobicity of the surface. The well-known, low cost copper electroplating process on the steel surface has been modified to achieve a hierarchical micro/nano scaled surface structure. The significantly reduced wettability of the coating surface in combination with biocidal activity of copper increases the surface resistance to biofouling. The influence of selected electroplating parameters in combination with the pretreatment of the substrate steel surface was investigated. The resulted coating surface was tested for durability under slurry flow conditions. Finally, the large component – the intake water filter of hydropower plant - was subject of field testing and was successfully tested for biofouling resistance.

Keywords: freshwater antifouling, copper coatings, superhydrophobicity, water filters

1 Introduction

Biofouling is a phenomenon in which the surfaces in contact with untreated water are inhabited by macro- and microorganisms: bacteria, algae barnacles, mussels etc. Fighting biofouling is a common challenge for people supervising the effective operation of hydrotechnical devices located in biologically contaminated freshwaters of rivers and inland reservoirs.

Hydrotechnical devices of hydropower, thermal power plants, industrial water intakes, water plant facilities such as water intake filters, heat exchanger piping [1], grating etc. drawing water from freshwater reservoirs are particularly susceptible to macro fouling (ex. algae or dreissenid mussels). Water intake inlet components such as inlet filters or cooling systems must undergo costly maintenance services - usually the mussels are mechanically detached from the steel surface. It is worth noting that the functionalities of hydrotechnical devices are affected by the reduced effective flow area on the filter screens - Figure 1 - and the lack of full closing capacity on the edges of gate valves.

Figure 1: Water inlet filter screen in hydropower colonized with Zebra mussels.

The technical and economic implications of biofouling in industrial water systems can be very serious.

Deterioration of the functionality of devices or its mechanical blockage may even lead to failure of the entire system. That results in the need for more frequent inspection and maintenance of the equipment. A significant part of the available literature on biofouling of energy devices addressed to is devoted to the economic losses caused by this phenomenon. Estimated average costs for one day of unplanned outage of a 235 MW(e) power plant may reach 0.3% of the earning and the costs of macro fouling organisms remove from screening housing in power plants are reported to reach USD 25.000–30.000 every 2 years [2].

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Of the many species of organisms, that cause biofouling, the *Dreissena Polymorpha* (Zebra mussel) has become the major and the most troublesome macro foulant in freshwater cooled systems. In recent years, a significant increase of the population of these species has been observed – starting from north-west Russia, through central and western Europe, Scandinavia, Great Britain, and Ireland. Due to global warming, mussels can reproduce at greater rates. *D. Polymorpha* is found almost everywhere in Poland, but its distribution is uneven. In northern Poland it occurs in lagoons, lower stretches and estuaries of the Vistula and Oder, most lakes of the main lake districts (Pomeranian Lake District – 95 %, Masurian Lake District – 78%) and particularly in large, deep lakes and small, pristine river [3]. In central Poland, *D. Polymorpha* is abundant in artificial and natural reservoirs of a lowland rivers, in the estuaries of rivers to these reservoirs, and in oxbow lakes. The observed expansion of *D. Polymorpha* in inland waters has a large technical and economic impact on raw-water dependent infrastructures, including power installations.

In April 2014, the European Parliament approved new legislation [4] to stem the spread of invasive species and drew up the ”black-list” of 50 such species, including *D. Polymorpha*.

The prevention of biofouling, and in particular the development of antifouling coatings has a long history. Most of investigation efforts in this area focus on shipping vessels, oceanographic sensors and aquaculture systems, offshore structures, seawater pipelines systems and heat-exchanger piping in desalination and power plants – meaning that most of them are dedicated to sea water structures.

The marine environment is relatively little threatened by toxic means of protection of structures due to the large area of circulating water reservoirs and, as a result, negligible impact on the environment. The known, low cost and very effective method of combating the biofouling of microorganisms such as barnacles and mussels is the use of biocides. The another known antifouling technology is the use of special paints and coatings [5-9]. Until recently, paints containing biocides compound tributyltin (TBT) and triphenyltin (TPT) have been used. However, it is largely limited due to Directive 76/769/EC and in fact – prohibited in the freshwater systems.

There is an exception for copper; according to European Commission Decision No. 2014/395/UE biocidal products containing copper are admitted using for anti-fouling protection. Considering the environmental impact, three main approaches for fouling-resistant surfaces development are presently used:

a) **Biocidal coatings**: technology based on the controlled release of authorized biocides, to kill the colonizing organisms. The most common type of these coatings are copper-based surface paints, which leach the biocide into the water to repel organisms.
b) **Fouling-release coatings**: technology based on physicochemical properties of the surface (low surface energy, smooth surface, low friction), used to prevent organisms from settling and to reduce their adhesion to the substrate by reducing the adhesive forces. These types of coatings available on the market are the surface paints based on silicones or fluoropolymers (for example

BIOCLEAN, Intersleek® 900). Their disadvantage is low mechanical strength and susceptibility to tearing off and abrasion.

c) **Surface engineering**: the appropriate combination of surface morphology in the micro and nano scale for creation of superhydrophobic features, which results an extremely low adhesion of living organisms.

Protective coatings such as epoxy resin or other anti-corrosion and anti-abrasion agents are not considered effective against settling of the mussels.

The novel antifouling coating presented in the study uses direct deposition of copper on the steel surface with electroplating. In addition to the known biocidal properties of copper, it introduces a two-scale micro/nano surface roughness to obtain an extremely low surface energy, and thus extremely low wettability. This solution effectively prevents the macrofouling organisms against settlement – including clams and mussels.

1.1 Surface hydrophobicity - theoretical background

Settlement of the mussels can be made considerably more difficult by making settlement surface superhydrophobic (with very low wettability). The wettability of the surface has been studied since the beginning of the 19th century. Young's model was formulated first and concerned the wettability of a smooth surface [10]. It describes the behavior of a drop of a water deposited on a smooth surface depending on the type of substrate material. The basic measure of wettability is the contact angle (CA), denoted as θ in Figure 2a. The geometry of the droplets contact with the surface is determined by the surface energy of the material: for poorly wettable surfaces it is relatively low. For the smooth, ideal surface, CA is defined by the Young's equation, which assumes the equilibrium of interfacial tension between solid, liquid and gas phases:

$$cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (1)$$

where:

θ - CA defined for Young model;
γ_{SG} - solid-gas interfacial tension;
γ_{SL} - solid-liquid interfacial tension;
γ_{LG} - liquid–gas interfacial tension.

If CA is < 90^o, the surface is hydrophilic, and if CA is > 90^o that is called hydrophobic. For CA > 150^o we are dealing with the phenomenon of superhydro-phobicity.

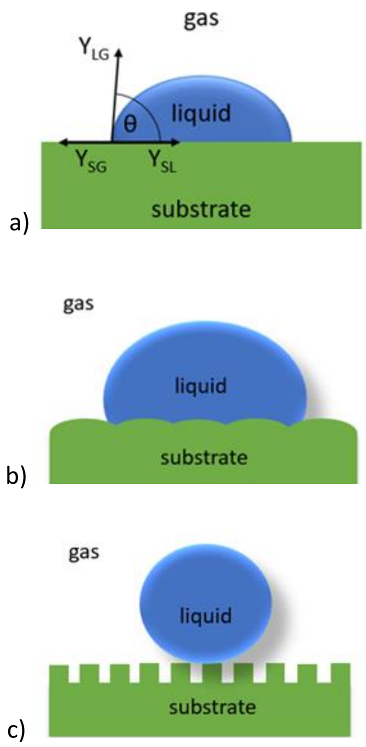

Figure: Liquid droplet on a flat smooth substrate (a), rough substrate (b) and nano-structured substrate (c).

The roughness of the substrate surface can significantly affect a its wettability features, enhancing the hydrophobic effects as shown on Figure 2b and Figure 2c. Depending on the surface morphology, a drop deposited on it may wet entire contact surface or part of it. These different modes of contact were defined by Wenzel [11] - see Figure 2b and supplemented by Cassie and Baxter [12] – see Figure 2c.

In the Wenzel model, the surface roughness r_f is defined as the ratio of the actual surface in contact with the fluid to its projection on the horizontal plane. For models that consider the surface roughness, the hydrophobicity metric is defined as the apparent contact angle (ACA) and differs from the

CA defined for perfectly flat surface. In the Wenzel model ACA (marked as θ_W) is defined as below:

$$cos\theta_W = r_f cos\theta \qquad (2)$$

A Cassie-Bexter model introduces a hierarchical micro/nano roughness surface structure – Figure 1c: the droplet is suspended on the tops of asperities (nano-sized) and two phases on the surface appear. The effect of such surface morphology was explained and described on the example of the lotus leaf by Bertholott and Neithuis [13]. In practice, pure Cassie-Baxter or Wenzel wetting models are rarely used because usually a droplet only partly wets the sides of a surface micro-cavities. This issue was discussed in papers [14-15]: the fraction of the wetted surface to its perpendicular projection was introduced into the metric: the corresponding apparent contact angle ACA was denoted by θy^* in the expression for ACA took the form:

$$cos\theta y^* = r_f f cos\theta_1 + (1-f)cos\theta_2 \qquad (3)$$

where:

f - fraction of the projected area of a substrate surface that is wetted by a liquid,
r_f - roughness ratio of the wetted area,
θ_1 – CA for a substrate,
θ_2 – CA for a substance, which fills the micro-cavity.

1.2 Antifouling technology concept

The superhydrophobicity of the surface obtained thanks to introduction of micro cavities has been noticed as a valuable extension of biocidal properties of copper. In further research it was assumed that the above-mentioned theory of surface wettability allows to control the colonization ability of mussels on hydrotechnical structures and devices. the concept of copper electroplating of those structures was investigated. For this purpose, the possibility of electroplating steel surfaces with copper with the option of obtaining a surface with predefined micro and nano-sized structure was investigated.

2 Technology description

The well-known and low-cost technology electrodeposition of copper on steel substrate has been modified in order to obtain the desired topological features of surface. It can be used to make uniform coatings regardless of the size and shape of the surface [16]. The expected topological features of nanostructured copper coating (**n**anostructured **Cu**) were achieved through a combined mechanical and electrochemical treatments.

Template-assisted electrodeposition has been utilized previously to obtain the coating surface with a patterned layer of metal deposit [14,15,17]. In this approach, the texture of the deposit depends on the structure of the template and may be adversely affected by the manufacturing of the template. For this reason, template-free electrodeposition methods have gained more interest and application [18-21]. Surface morphological instabilities were obtained by applying an appropriate overpotential or current density. Layers made by this method are mechanically durable, and their effective service life is expected to exceed five years [22].

2.1 Steel surface pre-treatment

The regular material used for hydrotechnical device manufacturing is 300 series stainless steel. It is well known that direct copper coating of that kind of stainless steel is difficult due to the very poor adhesion between the Cu layer and the substrate. This is due to the presence of a thin, impenetrable oxide film on the surface of the stainless steel.

For this reason, stainless steel must be properly pre-treated prior to copper electrodeposition. In the first step, the steel surface is cleaned in an alkaline solution, activated in an acid solution, and rinsed. Then, to increase the Cu layer adhesiveness, a thin nickel backing called nickel strike is deposited. As a result, a thin intermediate nickel "bridge" layer is obtained, which has a very good adhesion properties to both steel and copper.

2.2 **nCu**-coating deposition

The research was inspired by Cassie-Baxter's theory of hydrophobicity and its followers, in which the dependence of ACA on the wetted surface of micro cavities were examined. In the developed novel approach to obtaining superhydrophobicity features, the concept of hierarchical micro- and nano-structuring of the Cu coating surface was implemented.

Two-series of tests were carried out on reference samples for coatings deposited in bath using classic, industrially used, electrolytes. The first series of tests included the deposition of Cu in copper sulphate bath. The process was carried out at current density of 3 A/dm2 for 900 s. The second series of experiments was carried in a copper cyanide bath at a current density of 2 A/dm^2 for 3600 s. Following, the structure of the obtained surface, its wettability, wear resistance and anti-fouling properties were examined.

3 Results and discussion

3.1 Structure and wettability of **nCu** coating

The surface hydrophobicity features were identified by CA measurements on a dedicated laboratory rig. The surface morphology was examined using the HITACHI scanning electron microscope (SEM).

In the case of the coating applied after the sulphate bath using the current of 3 A/dm^2 during 900 s, the two-scale structure was not obtained. The obtained values of the contact angle ranged from 114^o to 120^o, but some hydrophilic areas were also observed on the surface of the samples. The surface topography in the SEM images indicated a coarse-crystalline structure with micrometric crystals size – Figure 3.

For the coating deposited from cyanide bath at 2 A/dm^2 in 3600 s, a fine-grained crystal structure was obtained. A hierarchical dendroid structure with a dual micro/nano size was obtained – Fig.4. The CA measurement showed superhydrophobic properties on the entire surface of the sample and amounted as much as 154^o - Fig. 5.

a) b)

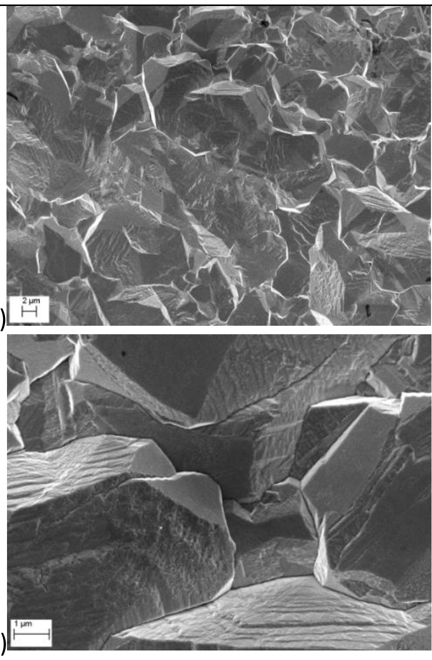

Figure 3: SEM images of the sample surface deposited from sulphate bath for current density of 3 A/dm2 in 900 s: a) mag. of 5000 x; b) mag. of 25000 x.

a) b)

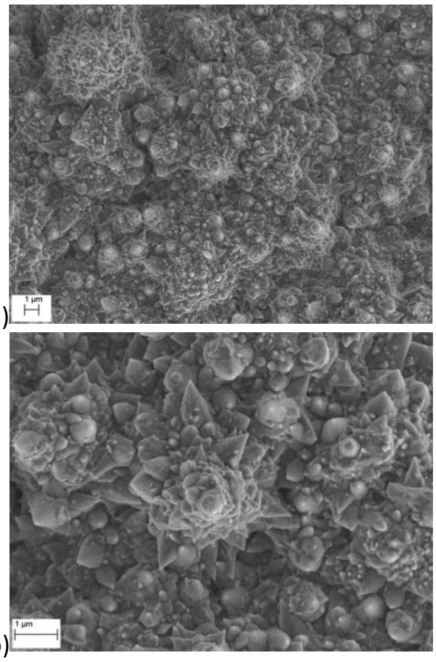

Figure 4: SEM images of the sample surface, deposited from cyanide bath for current density of 2 A/dm2 and in 3600 s : a) mag. of 10000 x; b) mag. of 30000 x.

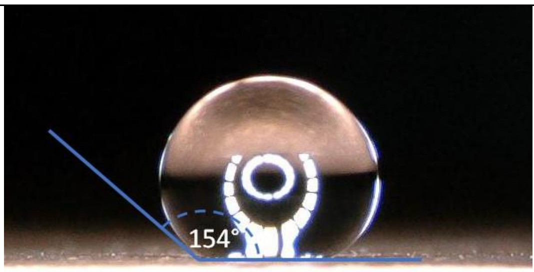

*Figure 5: Water droplet on the **nCu** coating obtained by electroplating from a bath in a cyanide solution – ACA observed.*

3.2 Wear resistance of **nCu** coating

Durability and abrasion resistance of antifouling coatings is one of the most desirable features in hydrotechnical applications. The resistance of the coating to mechanical peeling is particularly important, when water flowing through the hydrotechnical device contains inorganic particles such as sand or gravel.

However, an objective comparison of the abrasion resistance of superhydrophobic surfaces is hampered by the lack of a single, standardized test method. Most researchers use built in-house apparatus using various methods of mechanical abrasion as well as different criteria for assessing the change in surface hydrophobicity change. The detailed overview of recent advances in mechanical durability of superhydrophobic materials is presented in [23].

The operation conditions of hydrotechnical devices in a hydropower plant are specific: raw water may contain significant amounts of sand, gravel carried along with river debris. Testing the resistance of the developed coating to contact with material carried by raw water required the design of a dedicated test stand and test method. The design of the test rig was based on the idea presented in the paper [24] according to scheme shown in Figure 6.

The **nCu** coatings were subjected to a wear test in conditions like natural. The tested samples of stainless steel coated with developed **nCu** coating were used as paddles rotating the water corundum suspension. The slurry moved in this way caused abrasion of the surface of the paddles acting on it. The rotational speed was selected to reflect the flow conditions through the slot filter, i.e. velocity of inflow onto the sample was V ≈ 1.9 m/s .

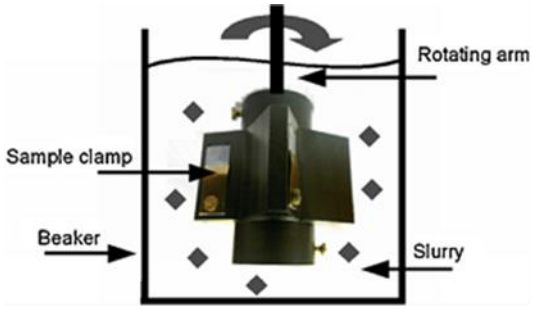

Figure 6: Rotary abrasive slurry test setup [26].

The slurry used for the abrasion tests was a 10% solution of the abrasive particles in water. To reproduce the realities of the operation of hydrotechnical devices, the abrasive additive in the slurry was composed as a mixture of sand (grain size < 50 µm) and electrocorundum (grain size < 100 µm) in a weight ratio 50:50. The progress of surface damage resulting from direct contact of slurry solid particles with the paddles surfaces was observed. The test lasted 48 h. The surface morphology of the samples was examined on SEM before and after the test as well as contact angle CA was measured to assess the wettability. A reduction in the roughness of the samples was observed and, consequently, a decrease in CA from the mean initial value of 154° to the mean of 110° after the end of the test. No peeling of the nCu surface was observed.

The results of the nCu abrasion test confirmed the good wear resistance of the superhydrophobic coating, with simultaneous increase in its wettability.

3.3 Antifouling features assessment

The key feature of the presented **nCu** coating is its antifouling. Its effectiveness was assessed step by step: from laboratory desktop experiments and ending with tests in industrial conditions.
The preliminary assessment of antifouling properties with **nCu** coating was carried out in laboratory conditions:

– in the university laboratory tests of samples with the **nCu** coating in aquarium were carried out by observing the migration and settlement of the *D.Polymorpha* mussel in the reproductive cycle;

steel samples without **nCu** coating were tested simultaneously as reference sample,

– at the university's experimental facilities at the stand in the Włocławek Reservoir on the Vistula river, where the *D.Polymorpha* population is particularly large. The samples were placed under water from the beginning of July to the end of September, i.e. during the period of natural settling of *D.Polymorpha* in a fresh water environment. For reference purposes, samples made of AISI 304 stainless steel and PVC were tested simultaneously.

The results of the laboratory biological tests were positive: mussels *D.Polymorpha* did not colonize the samples with the **nCu** coating, while on the samples without the coating, the large colonies of mussels were observed.

Final tests under industrial conditions were carried out in the Żarnowiec hydropower plant under normal operating conditions. This plant uses a slotted screen water filters at a turbine water intake – Figure 7a.

Water flow through the filter is relatively slow so the opportunity for mussels settling in the cartridge slotted screen is good and reported by plant operator. To validate novel **nCu** technology, the filter manufacturer PFTechnology Sp.z o.o, provided the full scale, AISI 304 stainless steel filter cartridge for testing purposes. The cartridge slotted screen – Figure 7b, was coated with **nCu** layer. The testing period was selected to cover the full reproductive and colonization cycle of the *D. Polymorpha* mussel.

The filter prototype test lasted 24 months between October 2018 and October 2020. The filter worked continuously under normal operating conditions, and it was monitored. In October 2020, after 24 months of operation, the filter prototype was disassembled, cleaned and filter cartridge was assessed for abrasion and biofouling.

a)

b)

Figure 7: a) Turbine water intake installation in Żarnowiec hydropower plant, b) The prototype of filter cartridge made in the developed nCu technology. Curtesy of PGE EO EW Żarnowiec and PFTechnology

The examination showed no trace of mussels and filtering screen surface of cartridge was covered only with sludge - Figure 8a. For reference purposes, the same type of filter cartridge working in a parallel pipeline was examined, but cartridge screen was not coated with the discussed **nCu** coating as usual numerous colonies of mussels were observed on its slotted screen - Figure 8b.


a)


b)

*Figure 8: Filter cartridges after operational test: a) cartridge with **nCu** coating, b) standard cartridge without **nCu** coating.*

4 Conclusions

The research confirmed the effectiveness of the application of the technology, in which the antifouling property of steel hydrotechnical devices operating in fresh water is obtained through the use of a copper electroplating process that allows obtaining superhydrophobic morphology of the surface. The superhydrophobicity of the surface, combined with the natural biocidal property of copper, made it possible to obtain an effective antifouling property for fresh water environment; the particular objective of research was protection against *Dreissena Polymorpha* colonization:

a) The biological assessment carried out on laboratory scale as well on field tests proved that the new **nCu** coating is well resistant against colonization by *D. Polymorpha*. The results of long-term operational tests in an industrial environment (intake filter in a hydropower plant) fully confirmed the laboratory results: the observed screen of the filter cartridge was free from mussels after a 24-month period of operation.
b) The number of hydrotechnical devices of hydropower are made of 300 series stainless steel. From a maintenance point of view, good adhesion of the copper coating to this type of steel is essential. To obtain expected durability of **nCu** coating on the stainless substrate, the stainless-steel substrate was pre-treated with a nano-sized layer of semi-precious metal. Laboratory wear tests under slurry conditions and tests under the operational conditions of a hydropower plant confirmed the lack of peeling as well as good durability of the **nCu** deposited on the substrate treated in this way.
c) Wear resistance of nCu showed normal level of degradation for that kind of devices operating under industrial conditions.

The developed **nCu** antifouling technology is low cost, environmentally friendly, including the technology process and relatively simple, compared to the ones used so far. It is particularly useful and recommended for antifouling protection of devices in hydro plant facilities as well on conventional power plants with open circuit water cooling systems when conventional antifouling biocides cannot be used due to environmental protection requirements. When maintenance is considered, **nCu** also eliminates the difficult and costly mechanical cleaning of mussel-infected hydro devices.

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