

CORROSION RESISTANCE AND ANTIFOULING
PERFORMANCE OF SELECTIVE PLATED NICKEL-BASED
COATINGS WITH SILVER PARTICLES

Radostina Yankova[✉], Ivan Rusev

Received on January 22, 2025

Presented by Ch. Roumenin, Member of BAS, on February 25, 2025

Abstract

This study presents preliminary findings on the corrosion resistance and antifouling properties of selectively electroplated composite nickel coatings embedded with silver particles. A comprehensive characterization was performed, encompassing qualitative X-ray phase analysis and electrochemical corrosion rate measurements. The antifouling performance of the coatings was assessed by monitoring biofouling levels in a controlled laboratory marine environment, with results validated through a 12-week exposure to a natural marine setting. The results demonstrated the successful integration of silver particles into the nickel matrix, significantly enhancing corrosion resistance. The embedded silver microparticles provided direct antibacterial activity, effectively inhibiting biofilm formation in the early stages. Throughout the observation period, no biofouling was detected on the coatings under either laboratory or natural conditions. A slight dull surface discolouration was observed, attributed to the oxidative interactions between silver, nickel, and seawater.

Key words: antifouling, selective plating, silver particles, nickel coatings, corrosion resistance

Introduction. The maritime industry plays a crucial role in global economy, facilitating the transportation of goods, resource extraction, and recreational activities. However, biofouling on submerged surfaces caused by marine organisms poses significant challenges, increasing ship weight and hydrodynamic resistance,

thereby raising fuel consumption and maintenance costs. Moreover, biofouling accelerates metal corrosion, leading to billions in annual financial losses and exacerbating environmental issues such as pollutant emissions and global warming [1–5].

Antifouling coatings are a widely used strategy to combat biofouling. Although effective, biocidal coatings release harmful substances that pose a threat to marine ecosystems. Copper-based coatings are also effective but face regulatory restrictions due to the release of copper ions [6–9]. Silicone and fluoropolymer coatings are more environmentally friendly alternatives; however, they offer limited effectiveness and require frequent maintenance [10–12].

Nickel-based coatings are highly regarded in marine applications due to their mechanical strength, corrosion resistance, and durability in harsh environments. They provide protection against seawater corrosion and enable the incorporation of antifouling agents such as silver particles to combat biofouling. Due to their superior adhesion and wear resistance, nickel coatings extend the service life of marine equipment [13–15]. Techniques such as plasma spraying, electroplating, and selective plating allow for precise application, addressing specific marine challenges [16–18].

Among the various coating techniques, selective plating is notable for its precision, ability to deposit coatings on localized areas, and minimal material waste. Selective plating enables the controlled deposition of nickel-based coatings, ensuring uniform thickness and strong adhesion to the substrate. This method also facilitates the incorporation of silver particles, which provide significant antimicrobial properties, thereby reducing biofouling and extending the operational lifespan of marine structures. The synergy between nickel's durability and silver's antimicrobial efficacy makes this approach a promising avenue for developing advanced, environmentally sustainable antifouling coatings.

This paper presents preliminary findings from a study investigating the antifouling properties of a novel nickel composite coating embedded with silver particles, fabricated using the selective plating method. The corrosion resistance and antifouling performance of the coatings were assessed under controlled conditions in a laboratory seawater pool and a natural marine environment. The results underscore the potential of these coatings as a sustainable and effective solution to biofouling challenges.

Materials and methods. In this study, two types of coatings – pure nickel and nickel-silver composite – were electroplated onto phosphor bronze (CuSn_5) test specimens using the selective electroplating method described in [19]. The bronze samples were initially cut into dimensions of 25×15 mm using a DTQ-5 low-speed precision cutting machine. The surfaces were then sequentially ground using silicon carbide (SiC) grit paper in grades P240, P400, P600, and P800, followed by polishing with a $1/4$ μm diamond suspension to achieve a smooth finish.

Before electroplating, the specimens underwent a series of preparatory treatments, including electrocleaning, etching, and surface activation, using standard electrolyte solutions suitable for the substrate material. Nickel deposits were electroplated using an electrolyte composed of 10 wt.% nickel formate, 20 wt.% nickel sulphate, 5 wt.% citric acid, and 1 wt.% aluminium sulphate. For the Ni-Ag composite coating, 2 wt.% silver powder (with particle sizes ranging from 3 to 5 μm) was added to the nickel electrolyte. The thickness of each electroplated coating was 20 μm .

X-ray diffraction (XRD) analysis was conducted using a TDM-10 Tongda diffractometer equipped with $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.54056 \text{ \AA}$). XRD patterns were recorded in a 2θ coupled scanning mode over the angular range of 20° – 90° , ensuring comprehensive phase identification. The resulting diffraction peaks were analyzed and compared to standard patterns using X'pert HighScore Plus software, enabling phase identification and providing insights into the crystalline structure of the coatings.

The corrosion resistance of the coatings was assessed using a Corrtest CS350 potentiostat/ galvanostat. Electrochemical corrosion tests were performed in a three-electrode configuration, consisting of a platinum (Pt) counter electrode, a reference electrode (Ag/AgCl silver/silver chloride), and the test sample with the coating as the working electrode. A 3.5% wt. sodium chloride (NaCl) solution was used as the corrosive medium, with the exposed surface of the sample limited to 1 cm^2 .

Open circuit potential (OCP) measurements were conducted to monitor the stability of the coatings in the corrosive medium over time. The OCP data provided insights into the thermodynamic tendency of the coatings to corrode. After OCP stabilization, potentiodynamic polarization tests were performed to evaluate the corrosion rate and resistance of the coatings. Tafel curves were obtained by sweeping the potential at a rate of 1 mV/s from -120 mV to $+120 \text{ mV}$ relative to the OCP. Key corrosion parameters, including corrosion potential (E_{corr}) and corrosion current density (I_{corr}), were extracted by fitting the Tafel plots. These parameters enabled a quantitative comparison of the corrosion resistance between the pure nickel and nickel-silver composite coatings.

To evaluate the biofouling resistance of the coatings, both pure nickel (Ni) and nickel-silver composite (Ni+2%Ag) coatings were tested in laboratory and natural marine environments. These experiments aimed to monitor the coatings' ability to resist biofilm formation and microfouling under both controlled and real-world conditions.

In the laboratory setup, experiments were conducted in a 30-liter aquarium containing seawater sourced from the Black Sea region near Varna, Bulgaria. A controlled marine ecosystem was established, including algae, mussels, and small marine organisms typical of the Black Sea. The samples were immersed in the aquarium for 12 weeks, with environmental parameters carefully controlled. The

temperature was maintained within the range of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$, seawater salinity ranged from 15 to 17 ‰, and pH was kept between 7.8 and 8.0. Oxygen saturation was maintained using an aerator, and seawater circulation was provided by a peristaltic pump operating at a flow rate of 300 mL/min, cycling every 24 hours. Every 10 days, one-third of the seawater was replaced with fresh seawater to maintain water quality. Visual observations and quantitative analysis were employed to assess the biofouling resistance. The extent of newly grown fouling areas was calculated relative to the total coated area.

To validate the laboratory findings, the coatings were also subjected to a 12-week field test in the natural marine environment of the Black Sea, near Varna, Bulgaria. The sample was immersed at a depth of approximately 500 mm and fixed in a silicone frame with the tested surface oriented horizontally to enhance gravitational adhesion and promote biofouling. The water temperature ranged from $21\text{--}23^{\circ}\text{C}$ at the start of the study (September 2024) to $10\text{--}12^{\circ}\text{C}$ by its conclusion (December 2024). The measured pH values of the water were between 8.1 and 8.3.

Results and discussion. XRD analysis. The X-ray diffraction patterns (Fig. 1) show clearly pronounced peaks of Ni in the nickel coating and Ni and Ag in the coating with added particles. Detailed information on peak parameters in terms of intensity, distance between crystallographic planes (d-Spacing), angle between the transmitted and reflected beam (2Theta), Miller indices of the crystallographic plane (hkl) and full width at half maximum of the peak (FWHM) obtained from the diffractograms of the coatings are presented in Fig. 2. For phase identification, the COD database with numbers 96-901-1604 and 96-901-1609 was used.

The results confirm the thesis that the selective electrochemical deposition technology is suitable for the formation of nickel composite coatings with added Ag particles.

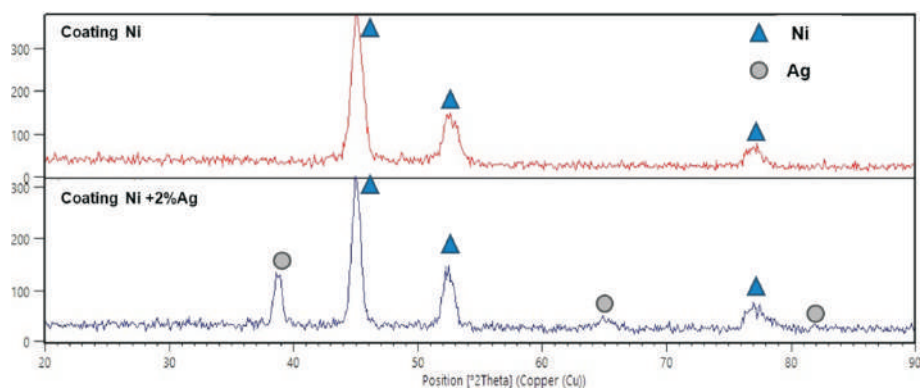


Fig. 1. XRD analysis of nickel coating (Ni) and nickel coating with added 2% Ag (Ni+2%Ag)

Coating Ni						Coating Ni+2%Ag					
No	Inten sity [%]	d- Spaci ng [Å]	2Thet a [°]	HK L	FW HM	No	Inten sity [%]	d- Spacin g [Å]	2Thet a [°]	HK L	FWH M
1	100	2.009 6	45.08	1 1 1	1.04	1	36.51	2.3238	38.72	1 1 1	0.7
2	31.43	1.739 1	52.58	0 0 2	1.43	2	100	2.0127	45.00	1 1 1	0.81
3	18.54	1.233 7	77.27	0 2 2	0.73	3	37.77	1.7443	52.41	0 0 2	1.01
						4	6.25	1.4338	64.99	0 2 2	1.6
						5	15.94	1.2359	77.10	0 2 2	1.6
						6	4.53	1.1714	82.23	2 2 2	0.27

Fig. 2. Peak parameters in terms of intensity, distance between the crystallographic planes (d-Spacing), angle between the transmitted and reflective beam (2Theta), Miller indices of the crystallographic plane (HKL), and full width at half maximum of the peak (FWHM) derived from the diffractogram obtained from the selective plated coatings

Corrosion resistance. To assess the corrosion resistance of the coatings, an open circuit potential (OCP) measurement was performed. The tests were carried out in a 3.5% sodium chloride (NaCl) solution at room temperature using a three-electrode configuration described in the “Materials and methods” section. The measurements were made for a period of 120 minutes to ensure potential stabilization and to record the equilibrium OCP. The OCP values of the coatings were analyzed to assess their thermodynamic tendencies towards corrosion. The results show that the nickel coating with added silver particles (Ni+2%Ag) has a more positive OCP compared to the pure nickel coating (Ni), which is an indicator of better corrosion resistance. The difference in potential between the two coatings demonstrates the effect of the added silver particles, which increase the chemical stability of the coating. After stabilization of the OCP, potentiodynamic polarization tests were performed to assess the corrosion rate and resistance of the coatings. Tafel curves were used to derive basic electrochemical parameters: anodic (ba) and cathodic (bc) Tafel coefficient, corrosion potential (E0), corrosion current (i0), as well as corrosion rate. The results are summarized in Fig. 3.

The results show that the addition of 2% silver particles in the nickel coating significantly reduces the corrosion current (i0) and the corrosion rate, which confirms the improved corrosion resistance. The anodic Tafel coefficient (ba) is higher for the Ni + 2% Ag coating, which suggests a slower dissolution of the material in the anodic reaction. At the same time, the cathodic Tafel coefficient (bc) decreases, which indicates changes in the cathodic reactions, probably due to the antimicrobial properties of the silver particles. The corrosion potential (E0) for the Ni + 2% Ag coating is significantly more positive (−0.03974 V) compared to the pure nickel coating (−0.2807 V), which indicates a higher corrosion resistance in a marine environment. The addition of silver particles to the nickel

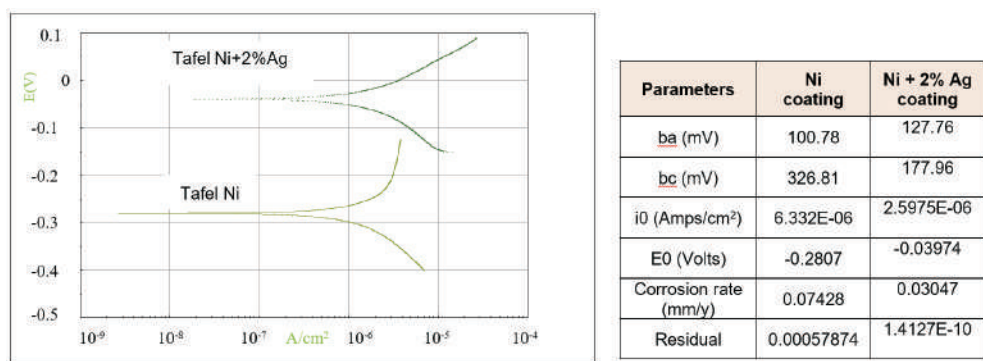


Fig. 3. Tafel curves and information from electrochemical parameters

matrix significantly improves the corrosion resistance and reduces the corrosion rate, which makes the Ni + 2% Ag coatings suitable for applications in aggressive marine environments.

Fouling tests. The process of biofouling formation in the laboratory pool and in the sea was monitored weekly. The results are presented in Fig. 4. The nickel coating with added silver particles showed excellent antifouling properties in laboratory marine conditions. For the entire period of stay in the laboratory pool of 12 weeks, no biofilm formation or microfouling were observed. No strong darkening of the surface was observed, which indicates that the coating forms a



Fig. 4. Ni+2%Ag coating after a stay in a simulated marine environment – aquarium (A); in a natural marine environment (S)

denser structure than pure nickel and prevents electrochemical corrosion of the bronze base and the formation of copper oxides on the surface of the samples, despite the small thickness of the coating of 20 μm . The weak overall graying of the surface is probably due to the participation of silver and nickel in oxidation reactions with seawater. Ni+2%Ag coating prevents biofilm formation even in the initial stages.

For a period of 12 weeks, no biofouling formation was observed on the Ni+2%Ag coating placed in a natural marine environment. It is clearly seen that after the first month, colour changes occur on the surface of the samples, more clearly expressed at the end of the second month, which indicates the occurrence of complex chemical and biochemical processes. The colour changes in the coatings are due to chemical reactions occurring on the surface of the metals under the influence of salt water, oxygen, organic materials and microbes in the Black Sea. The presence of microorganisms and the formation of biofilms in seawater can lead to the formation of diverse and complex chemical compounds, including organometallic complexes, causing a wide variety of processes – both destructive and corrosive, as well as protective and inhibiting fouling. The colour change to dark gray on the surface of the coating is probably due to the formation of Ag-O, as a result of the interaction with oxygen, as well as the formation of Ag-S as a result of the reaction of silver with sulphides from bacterial metabolites.

Conclusion. The selective electroplating method effectively produces stable composite coatings based on nickel with integrated silver particles. The incorporation of silver particles into the nickel matrix significantly enhances the coating's corrosion resistance and chemical stability, both of which are crucial for effective biofouling prevention. After a three-month operational cycle in a natural marine environment, the nickel-silver composite coating exhibited excellent biofouling resistance. This performance is attributed to the complementary roles of the coating's components: the nickel matrix provides robust mechanical and chemical stability, while the silver ions inhibit bacterial growth through their direct antibacterial activity.

The addition of silver particles induces characteristic surface chemical reactions, resulting in slight changes in appearance, such as graying, without compromising functionality. On the contrary, these reactions enhance the coating's performance. The silver microparticles effectively inhibit biofilm formation during the initial stages, ensuring that no fouling or biocorrosion processes occur on the surface.

These findings underscore the potential of nickel-silver composite coatings as a durable and effective solution for marine applications, combining strong mechanical properties with superior corrosion resistance and antifouling performance.

REFERENCES

- [1] LI L., H. HONG, J. CAO, Y. YANG (2023) Progress in Marine Antifouling Coatings: Current Status and Prospects, *Coatings*, **13**(11), 1893, <https://doi.org/10.3390/COATINGS13111893>.
- [2] SCHULTZ M. P., J. A. BENDICK, E. R. HOLM, W. M. HERTEL (2011) Economic impact of biofouling on a naval surface ship, *Biofouling*, **27**(1), 87–98, <https://doi.org/10.1080/08927014.2010.542809>.
- [3] LIU S., A. PAPANIKOLAOU, A. BEZUNARTEA-BARRIO et al. (2021) On the effect of biofouling on the minimum propulsion power of ships for safe navigation in realistic conditions, *Biofouling*, **37**(2), 194–205, <https://doi.org/10.1080/08927014.2021.1890044>.
- [4] HELLIO C., D. M. YEBRA (2009) *Advances in Marine Antifouling Coatings and Technologies*, Woodhead Publishing, Cambridge, 1–15, <https://doi.org/10.1533/9781845696313.1>.
- [5] SELIM M. S., M. A. SHENASHEN, S. A. EL-SAFY et al. (2017) Recent progress in marine foul-release polymeric nanocomposite coatings, *Prog. Mater. Sci.*, **87**, 1–32, <https://doi.org/10.1016/j.pmatsci.2017.02.001>.
- [6] TORNERO V., G. HANKE (2016) Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas, *Mar. Pollut. Bull.*, **112**(1–2), 17–38, <https://doi.org/10.1016/j.marpolbul.2016.06.091>.
- [7] GITTENS J., T. SMITH, R. SULEIMAN, R. AKID (2013) Current and emerging environmentally-friendly systems for fouling control in the marine environment, *Biotech. Adv.*, **31**(8), <https://doi.org/10.1016/j.biotechadv.2013.09.002>.
- [8] AMARA I., W. MILED, R. SLAMA, N. LADHARI (2017) Antifouling processes and toxicity effects of antifouling paints on marine environment. A Review, *Environ. Toxicol. Pharmacol.*, **57**, 115–130, <https://doi.org/10.1016/j.etap.2017.12.001>.
- [9] TAKAHASHI K. (2009) Release Rate of Biocides from Antifouling Paints. In: Arai T., Harino H., Ohji M., Langston W. J. (eds) *Ecotoxicology of Antifouling Biocides*, Springer, Tokyo, https://doi.org/10.1007/978-4-431-85709-9_1.
- [10] YEBRA D. M., S. KIIL, K. DAM-JOHANSEN (2004) Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings, *Prog. Org. Coat.*, **50**(2), 75–104, <https://doi.org/10.1016/j.porgcoat.2003.06.001>.
- [11] BRESSY C., A. MARGAILLAN, F. FAY et al. (2009) 18-Tin-free self-polishing marine antifouling coatings, *Advances in Marine Antifouling Coatings and Technologies*, 445–491, <https://doi.org/10.1533/9781845696313.3.445>.
- [12] LEJARS M., A. MARGAILLAN, C. BRESSY (2012) Fouling release coatings: A non-toxic alternative to biocidal antifouling coatings, *Chem. Rev.*, **112**(8), 4347–4390, https://doi.org/10.1021/CR200350V/ASSET/CR200350V.FP.PNG_V03.
- [13] POWELL C., H. T. MICHELS (2000F) Copper-Nickel Alloys for Seawater Corrosion Resistance and Anti-Fouling – A State of the Art Review, https://www.researchgate.net/publication/254544596_Copper-Nickel_Alloys_for_Seawater_Corrosion_Resistance_and_Anti-Fouling_-_A_State_of_the_Art_Review, (accessed April 25, 2024).

- [14] POWELL C. A. (1992) Cu-Ni Alloy Resistance to Corrosion and Biofouling, https://www.copper.org/applications/marine/cuni/properties/biofouling/resistance_to_corrosion_and_biofouling.html, (accessed April 25, 2024).
- [15] Corrosion resistance of copper-nickel alloys, <https://nickelinstitute.org/en/nickel-applications/copper-nickel-alloys/corrosion-resistance-of-copper-nickel-alloys>, (accessed November 29, 2024).
- [16] SADIKU-AGBOOLA O., E. R. SADIKU, O. F. BIOTIDARA (2012) The properties and the effect of operating parameters on nickel plating (review), *Int. J. Phys. Sci.*, **7**(3), 349–360, <https://doi.org/10.5897/IJPS11.1163>.
- [17] SKULEV H., D. VESELINOV (2022) The Influence of Steel and Cast Iron as Substrate Materials on the Microstructure, Microhardness and Wear Resistance of Nickel-base Ti-Al Plasma Spray Coatings, *C. R. Acad. Bulg. Sci.*, **75**(11), 1656–1662, <https://doi.org/10.7546/CRABS.2022.11.13>.
- [18] SKULEV H., D. VESELINOV (2022) The Influence of Substrate Materials on the Microstructure, Microhardness and Wear Resistance of Nickel-base Plasma Spray Coatings, *C. R. Acad. Bulg. Sci.*, **75**(9), 1343–1350, <https://doi.org/10.7546/CRABS.2022.09.12>.
- [19] VESELINOV D. (2021) The influence of voltage and anode jackets on the microstructure, microroughness and microhardness of cobalt coatings deposited on Ti-6Al-4V using brush plating, *Journal of the Technical University of Gabrovo*, **63**(11/2021).

Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre “Acad. A. Balevski”, Bulgarian Academy of Sciences, 67 Shipchenski Prohod Blvd, 1574 Sofia, Bulgaria

e-mails: radyankova@ims.bas.bg, rusev@ims.bas.bg