

Novel antimicrobial heat-conducting “metallic” coatings against biofouling and biocorrosion

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ABSTRACT

NiMo and NiMo with embedded CeO₂ nanoparticles (100 nm) were tested as antimicrobial coatings (~15 µm thickness) on Ti (titanium) surfaces using an electrochemical process for heat exchanger applications onboard marine vessels. Preliminary static biofouling and biocorrosion (also known as microbiologically influenced corrosion) assessments were carried out in glass bottles using pure-strain *Desulfovibrio vulgaris*, a sulfate reducing bacterium (SRB), in deoxygenated ATCC 1249 medium at 37°C, and using an alga (*Chlorella vulgaris*) mixed with general heterotrophic bacteria (GHB) in enriched artificial seawater at 28°C. It was found that NiMo/CeO₂ was much more effective than NiMo in preventing SRB biofilm formation with an efficacy of 99% reduction in *D. vulgaris* sessile cells after 21-day incubation. The NiMo/CeO₂ coating also exhibited a 50% lower corrosion current density compared to the uncoated Ti against SRB corrosion. Both NiMo and NiMo/CeO₂ coatings achieved 99% reduction in sessile algal cells. Confocal laser scanning microscopy (CLSM) biofilm images indicated a large reduction of sessile GHB cells. The CLSM images also confirmed the biocidal kill effects of the two coatings. Unlike polymer coatings, the “metallic” coatings are heat conductive. Thus, the corrosion resistant antifouling coatings are suitable for heat exchanger applications.

Keywords: Biofilm; Biofouling; Biocorrosion; Coating; Antimicrobial; Heat Exchanger

INTRODUCTION

Seawater biofouling is a major threat in heat exchanger operations. It decreases the heat transfer efficiency and service life of heat exchangers^{1,2}. The formation of deposits caused by biofouling on the heat exchanger metal surfaces increases surface roughness and decreases cross-sectional flow area, which leads to higher friction loss in fluid flow^{3,4}. Mitigation methods, including surface scrubbing, fluidizing bed heat exchangers, cleaning-in-place and dosing anti-fouling chemicals, are the main ways to tackle biofouling⁵. Conventional approaches to treat biofouled components by periodic electrochlorination or acid flushes are costly and environmentally hazardous. Huge costs are associated with heat exchanger biofouling losses, but there is still a lack of research to develop heat-conducting antifouling coatings to heat exchangers³.

Biofouling and biocorrosion are caused by unwanted growth of biofilms^{6,7}. Sulfate reducing bacteria (SRB), which can grow anaerobically beneath an aerobic or facultative biofilm, are the ubiquitous bacteria in biocorrosion^{8–11}. Ti (titanium) and Ti alloys have good mechanical properties, and high corrosion resistance due to the thin and dense oxidized films on the Ti surface that provide excellent passivation against corrosion^{12–14}. However, they are susceptible to biofilm coverage, and biocorrosion by sulfate-reducing bacteria (SRB) and other microbes^{14,15}. Ti heat exchanger tubing biofouling occurs naturally during open water-cooling operations on both military and commercial vessels^{4,16}. The cooling water side operating temperature range is typically less than 60°C, which is suitable for microbial growth¹⁷.

Seawater heat exchangers are plagued by biofouling which results in severe degradation of performances. Furthermore, heat exchanger failure can lead to ships being disabled. For example, USS Zumwalt (DDG class) broke down in the Panama Canal in 2016, presumably due to a heat exchanger failure and seawater leaks. It had to be towed to port. A protective coating is desired to resist biofouling and biocorrosion caused by microbial biofilms. Polymer coatings are a common approach to combat corrosion¹⁸. Antimicrobial agents can be blended into polymer coatings to mitigate biofilm formation. However, polymer coatings do not conduct heat well and their low erosion resistance is also a major problem¹⁹.

Nickel-molybdenum (NiMo) “metallic” coatings show excellent corrosion resistance in harsh environments, such as acidic, high temperature, high wear environments^{20,21}. Because of their superior hardness (1000 Knoop), good thermal conductivity (11.1 W/(m·K) vs. 16.0 W/(m·K) for titanium at 20°C)²², and high corrosion resistance in seawater environments, NiMo is a good choice as a metallic base coating material. The presence of Mo in 316 stainless steel (SS) has been found to inhibit the growth of SRB biofilms²³.

During heat exchanger operations in the field, mixed-culture biofilms form on tubing surfaces. The top layer of a biofilm is aerobic, but bottom tends to be anaerobic. A coating's resistance to SRB is important because SRB sessile cells live in the anaerobic niche directly on the base metal surface underneath the top biofilm²⁴. SRB cells produce highly reactive sulfide species that can react with biocidal metal ions²⁵. SRB are known to resist copper ion toxicity because their metabolic product H₂S can precipitate biocidal Cu⁺ and Cu²⁺ extremely well^{8,26}. Cu-bearing SS is very effective against *Pseudomonas aeruginosa* biofilm, but it has no efficacy against SRB biofilm formation^{27,28}. It was recently shown that when cerium element (in the form of CeO₂) was over 0.18 wt.% in Cu-bearing 2205 duplex stainless steel (DSS), the SRB

biofilm formation was inhibited effectively²⁹. It showed superior SRB resistance compared with 2205 DSS and 2205 Cu-DSS stainless steels without Ce. In this work, NiMo coatings with varying concentrations of biocidal CeO₂ nanoparticle inclusions were applied to grade 2 Ti substrate. The antifouling efficacies of the coatings were evaluated using sessile cell counts and Confocal laser scanning microscopy (CLSM) images after 21-d incubation in ATCC[†] 1249 culture medium inoculated with *D. vulgaris*, and 21-d incubation in enriched artificial seawater (EASW) inoculated with *Chlorella vulgaris* (a common algal species) mixed with general heterotrophic bacteria (GHB). Two best performing coatings were chosen for further evaluation using electrochemical tests for SRB corrosion resistance. An empirical biofouling resistance correlation was established using the new concept of biofouling resistance equivalent number (BREN).

EXPERIMENTAL PROCEDURE

Biocidal CeO₂ nanoparticles (100 nm) were incorporated within a metal (NiMo) matrix on Ti surface by electrocodeposition. The advantage of fabricating composites in this way is the ability to produce materials with very uniform particle dispersion within the metal matrix, owing to particle suspension in an aqueous solution that reduces their agglomeration³⁰.

Pulsed current (PC) was applied in the electrocodeposition process. In the PC scheme, the applied current was interrupted by an off-time, t_{off} , where typically open circuit potential (OCP) conditions were maintained. The PC scheme promoted a nanocrystalline structure in the NiMo, and CeO₂ inclusions that were less agglomerated in comparison to those observed under direct current (DC) mode. In this work, DC, high frequency PC and low frequency PC were used to produce different coatings. The FARADAYIC[‡] antifouling electrocodeposition process was utilized to apply NiMo-biocidal coatings directly to grade 2 Ti substrate³¹. Figure 1 shows the setup for the whole process.

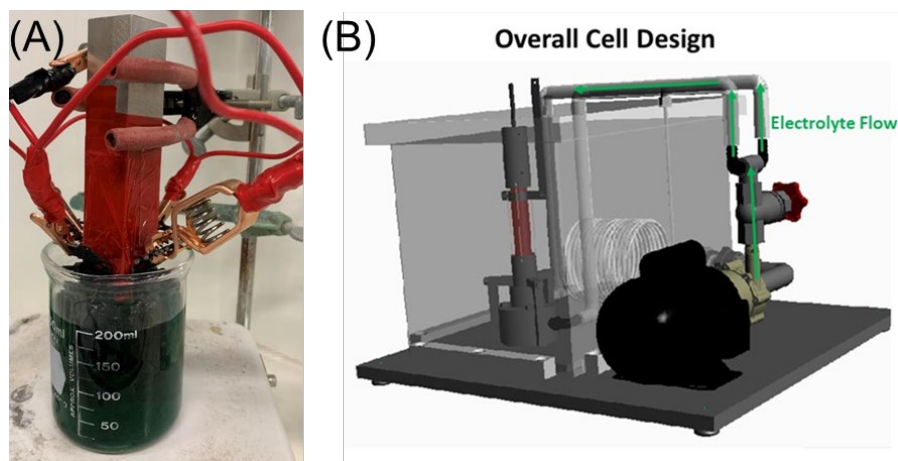


Figure 1. Setup for a rectangular Ti sample used for preliminary coating screening (A), and tool for applying a coating to Ti surface.

D. vulgaris, a commonly used SRB species for biocorrosion studies, was incubated anaerobically in 125 mL vials with 50 mL deoxygenated ATCC 1249 culture medium at 37°C for 21 days. The composition of ATCC 1249 medium was (g/L): MgSO₄·7H₂O 4.1, sodium citrate·2H₂O 5.7, CaSO₄·2H₂O 1.0, NH₄Cl 1.0,

K₂HPO₄, 0.5, sodium lactate 3.5, yeast extract 1.0, Fe(NH₄)₂(SO₄)₂·6H₂O 1.38. *C. vulgaris* mixed with GHB was incubated aerobically in 200 mL EASW in 450 mL glass vessels at 28°C for 21 d without. A lower temperature was used for better *C. vulgaris* growth. The abundant GHB in the mixed culture helped validate coating efficacy against biofouling bacteria other than *D. vulgaris*. The EASW composition was (g/L): Na₂SO₄ 3.91, NaCl 23.476, NaHCO₃ 0.192, KBr 0.096, KCl 0.664, H₃BO₃ 0.026, SrCl₂·6H₂O 0.040, MgCl₂·6H₂O 10.610, CaCl₂·2H₂O 1.469, yeast extract 1.0, tri-sodium citrate 0.5, sodium lactate 3.5, CaSO₄·0.5H₂O 0.1, NH₄Cl 0.1, MgSO₄·7H₂O 0.71, Fe(NH₄)₂(SO₄)₂·6H₂O 1.38, K₂HPO₄ 0.05.

The initial pH values of the culture media were neutralized to 7.0 by adding a 5% (w/w) HCl solution or 5% (w/w) NaOH solution for both cultures. The culture media and lab tools such as tweezers were sterilized in an autoclave for 20 min at 121°C. After autoclaving, the ATCC 1249 medium was sparged with filter-sterilized N₂ to deoxygenate for at least 1 h. One hundred ppm (w/w) L-cysteine was added to the ATCC 1249 culture medium as an oxygen scavenger to reduce dissolved oxygen further. Following EASW sterilization, deoxygenation was not needed for EASW because *C. vulgaris* growth was aerobic.

Table 1. Test matrices for SRB and alga

Microorganism	<i>D. vulgaris</i> (pure culture)	<i>C. vulgaris</i> (mixed with GHB)
Cultural medium	ATCC 1249 medium	EASW
Coupon	Ti coupons with and without antibiofilm coatings	Ti coupons with and without antibiofilm coatings
Cultural medium volume	100 mL in 125 mL anaerobic vials	200 mL in 450 mL glass bottles
Temperature	37°C (optimal for growth)	28°C
Incubation Time	21 days	21 days
Analysis	Cell counting and CLSM imaging	Cell counting and CLSM imaging

SRB planktonic and sessile cell counts were enumerated using a hemocytometer. For the SRB sessile cell counting, the biofilm covered coupons were first rinsed in pH 7.4 phosphate buffered saline (PBS) solution 3 times. The biofilm on each coupon surface was scraped off using a sterile brush into a 10 mL PBS solution. The cell suspension was counted under a hemocytometer. Although very small, *D. vulgaris* cells appeared as motile dots under a 400X light microscope. This more precise counting method yielded cell counts that were consistent with MPN (most probably number) results⁸. Eucaryotic *C. vulgaris* cells were seen as green dots under the light microscope (Figure 2). Unlike pure-culture *D. vulgaris* cells that are motile, mixed culture GHB cells in the algal culture could not be counted on a hemocytometer.

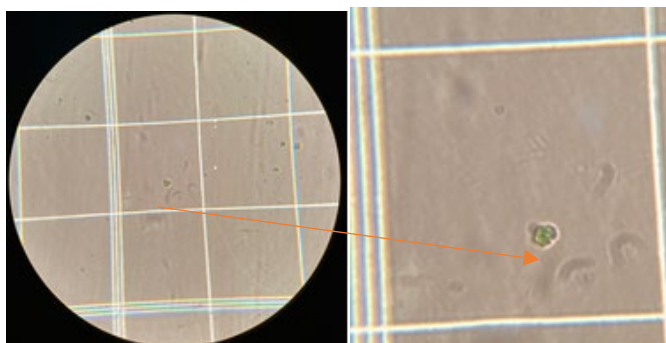


Figure 2. *C. vulgaris* eucaryotic algal cells showing unique green color (each hemocytometer square 0.05 mm × 0.05 mm).