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The Effect of Coating Propellers: the Impact on the Integrity of Nickel Aluminum Bronze as a Function of Cathodic Protection

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Scientific Report
DRDC-RDDC-2018-R154
August 2018

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Abstract

To investigate coatings-based methods for propeller biofouling mitigation, specimens of nickel aluminum bronze (NAB) were prepared by coating with either marine epoxy or copper ablative antifouling, and scored on each side, to expose the NAB. The specimens were immersed for 18 months in low flowing seawater, under either full or no cathodic protection. The specimens were assessed at 3, 6, 12, and 18 months; the assessment included the removal of a small cross section for microscopic examination. The integrity of the NAB at the crevices, due to the score lines, was monitored as a function of time. The coating condition was also monitored; the onset of copper conversion was noted by the 3 month mark with the protected antifouling coated specimens, and continued to increase with time. Furthermore, the electrodeposition of copper onto exposed NAB was also noted with protected antifouling specimens.

Significance to defence and security

Although the benefits of coatings propellers are numerous, and include drag reduction and reduced maintenance, it is important to ensure that coating of propellers will not impact the integrity of the propeller material. These experiments were designed to assess the long term effect of coating on the integrity of NAB; however, the experiments were concluded earlier than planned due to the closure of the Dockyard Laboratory Pacific (DLP).



Résumé

Dans le but d'étudier les procédés de revêtement pour atténuer l'encrassement biologique des hélices, on a préparé des échantillons de bronze au nickel-aluminium (BNA) en appliquant une couche antisalissure ablatrice à base de cuivre ou d'époxy marin. Les échantillons ont été entaillés de chaque côté afin d'exposer le BNA. On les a ensuite immergés pendant dix-huit mois dans de l'eau de mer à faible débit, avec ou sans protection cathodique complète, puis vérifiés après trois, six, douze et dix-huit mois, notamment en procédant à une petite coupe transversale afin de les examiner au microscope. L'intégrité du BNA, à l'emplacement des entailles, a été vérifiée en fonction du temps. On a également vérifié l'état des revêtements et constaté qu'une transformation du cuivre s'était amorcée après trois mois chez les échantillons protégés par un revêtement antisalissure et que celle-ci avait progressé au fil du temps. De plus, on a constaté l'électrodéposition du cuivre sur le BNA exposé chez les échantillons avec protection antisalissure.

Importance pour la défense et la sécurité

Les revêtements d'hélices offrent de nombreux avantages, entre autres parce qu'ils réduisent la résistance à l'écoulement et nécessitent moins d'entretien. Il importe toutefois de s'assurer qu'ils ne nuisent pas à l'intégrité des matériaux dont sont faites les hélices. Les expériences visaient à évaluer les effets à long terme des revêtements sur le BNA. Elles se sont néanmoins terminées plus tôt que prévu en raison de la fermeture du Laboratoire du chantier naval (Pacifique).



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Acknowledgements

The authors gratefully acknowledge helpful discussions and technical support from Yueping Wang and Kumar Sadayappan (Natural Resources Canada (NRCan)), Wayne Neil and Kate Dylejko (Defence Science and Technology Group (DSTG)), and Chris Bayley, Joel Higgins and Alexandra McLeod (Defence Research and Development Canada (DRDC)).



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1 Introduction

Nickel aluminum bronze (NAB) is commonly used for many applications in the marine realm, including propellers, due to its excellent wear, high strength, excellent corrosion resistance, high cavitation resistance, good stress corrosion properties, and high resistance to biofouling.

NAB is a complex copper (Cu)-based alloy typically containing 6–13% aluminum (Al), up to 7% iron (Fe) and 7% nickel (Ni), and up to 1.5% manganese (Mn), by weight [1]. The Al, Fe, and Ni improve the strength and corrosion resistance, and the Mn enhances strength and imparts oxidation resistance [1, 2]. The alloying elements are not uniformly distributed through the copper base, but exist in varying quantities within different phases of the microstructure. The microstructure can be controlled, to a degree, through composition, fabrication conditions (temperature), and subsequent heat treatment [1]. The prevalence and distribution of each phase has a significant impact on the overall properties of the alloy.

Figure 1 shows a scanning electron microscope image of NAB, denoting various phases. The α -phase is comprised mostly of copper and aluminum, and appears light in colour. The intermetallic κ -phases are rich in Ni, Al, and Fe (Table 1), and appear darker. The κ_I -phase is typically the large irregular-shaped globules (reported to be based on Fe_3Al [2]), and the κ_{II} -phase is typically the smaller irregular-shaped globules, or rosettes. The κ_{III} -phase exists as lamellar-shaped, or globular (degraded lamellar) precipitates in the eutectoid region, and the κ_{IV} -phase exists as small particles distributed throughout the α -phase [1, 2].

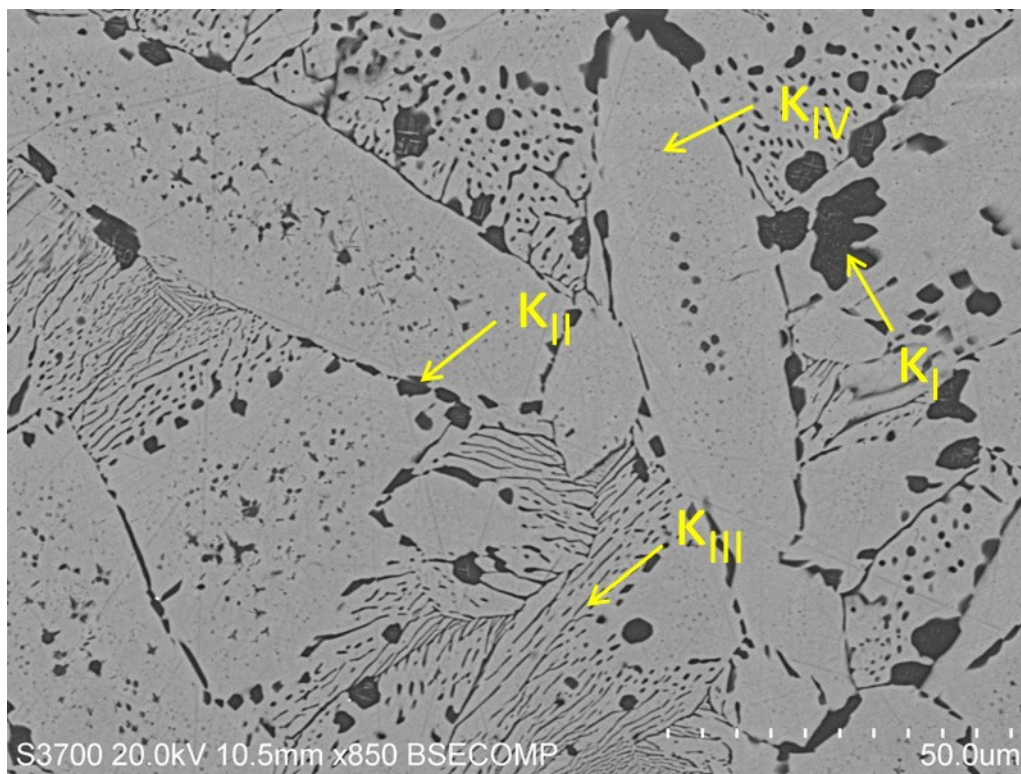


Figure 1: Scanning electron microscope image of NAB showing the Cu-rich α -phase and the different intermetallic κ -phases, denoted by yellow arrows.¹

Table 1: Energy Dispersive X-Ray Spectroscopic data of the phases present in cast nickel aluminum bronze.^a

| Phase | Alloy component (Weight %) | | | | |
|---|----------------------------|------|-------|-------|-------|
| | Al | Mn | Fe | Ni | Cu |
| α | 7.90 | 0.20 | 2.58 | 2.91 | 86.41 |
| β | 8.51 | 0.52 | 2.20 | 2.58 | 86.19 |
| κ_I | 17.35 | 1.25 | 35.69 | 18.07 | 27.64 |
| κ_{II} | 19.09 | 0.93 | 26.60 | 26.04 | 27.34 |
| κ_{III} | 18.87 | 0.45 | 12.86 | 26.80 | 41.03 |
| κ_{IV} | 8.12 | 0.84 | 42.70 | 35.32 | 13.01 |
| ^a Taken from Table 6, page 25 of ref [1] | | | | | |

¹ Although NAB having a greater proportion of Ni relative to Fe, typically does not exhibit the presence of κ_I -phase, in this work, elemental analysis of the large, globular phases shown in Figure 1 suggest that these are κ_I - not κ_{II} -phase.

1.1 Corrosion of NAB

NAB's corrosion resistance is attributed to the formation of a duplex oxide film comprised of copper (I) oxide (Cu_2O) and alumina (Al_2O_3). This very thin oxide layer adheres well to the NAB surface and is self-repairing, in the presence of oxygen. NAB that is immersed in oxygen-containing water will develop this oxide layer, which provides a barrier to ionic transport, significantly decreasing the rates of corrosion reactions [1, 2].

Although NAB exhibits high resistance to general corrosion, it is susceptible to pitting, galvanic corrosion, and crevice corrosion [1]. Pitting can occur in areas where the oxide film has been damaged, resulting in differential aeration, which causes an oxygen concentration cell. Galvanic corrosion occurs when the NAB is electrically connected to a more electropositive metal. Crevice corrosion can occur wherever an area of the substrate is covered by another material (crevice-former) and a thin film of liquid exists between the substrate and the material. The crevice former can be a coating, biofouling, or other material, including calcareous deposits².

Within a crevice, the mobility of species is restricted, and inadequate oxygen delivery can result in degradation of the protective oxide layer, resulting in crevice corrosion. The mechanism of crevice corrosion in NAB is a form of selective phase corrosion (SPC) [1]. The eutectic phase (or eutectoid), comprised of the Cu-rich α -phase interspersed with a lamellar Ni-Al-Fe-rich κ_{III} -phase, is susceptible to SPC under crevice conditions [1]. Initially, the α -phase is anodic relative to the κ_{III} -phase, with preferential corrosion of the α -phase ensuing at a low rate [3]. The crevice solution becomes acidic due to hydrolysis of metal complexes formed during the initial stage of SPC (corrosion of the α -phase) [3]. As the pH drops, the α -phase becomes cathodic, and selective corrosion of the κ -phases occurs. At this advanced stage of SPC, the copper ions present in the crevice solution undergo reduction and deposit onto the substrate. This copper re-deposition is effectively electrodeposition, and visible by eye, when a sufficient amount of copper has re-deposited.

Corrosion of NAB, either general corrosion or crevice corrosion, can be mitigated through cathodic protection (CP). NAB propellers that are electrically connected to the ship's hull, via shaft grounding systems, should be protected by the ship's CP system (either sacrificial anodes or an impressed current cathodic protection (ICCP) system). In the absence of a CP system, inadvertent propeller protection may also occur via galvanic coupling to the steel hull, to the detriment of the hull. Although the CP system should protect the NAB propellers (and the steel hull) from corrosion, events may arise in which the level of cathodic protection is inadequate, such as poor electrical connectivity (shaft grounding system) to the CP system, or the requirement for the CP to be turned off. In such cases, corrosion as noted above—pitting, crevice, and galvanic—will ensue.

1.2 Propeller Biofouling Mitigation

Although NAB exhibits resistance to biofouling as a result of the formation of copper ions created by slow dissolution of NAB in seawater [1], suppression of the formation of copper ions, via cathodic protection, diminishes NAB's natural biofouling resistance. This is not a huge issue for vessels which sail frequently, since the initial biofouling products (biofilm and slime) will be removed under the high shear conditions associated with sailing. However, it is a serious issue for vessels which sit alongside for extended periods of time. Figure 2 shows a propeller from a naval vessel that sat alongside for 18 months.

² Calcareous deposits form by the precipitation of calcium carbonate and magnesium hydroxide in seawater under alkaline conditions; the alkaline conditions are created by hydroxide production resulting from cathodic protection.

The biofouling is significant and covers all surfaces of the propellers. Mechanical means was necessary to remove the biofouling, ultimately risking damage to the propeller.



Figure 2: This vessel sat alongside for 18 months in Victoria, BC, resulting in significant biofouling of the propellers that required removal by mechanical means. Such mechanical methods increase the risk of propeller damage. Photo credit: S. McLaughlin, DRDC – Atlantic Research Centre.

In order to mitigate biofouling on vessels destined to sit alongside for extended periods, the propellers can be coated. The coating can be either a permanent coating, comprised of a complete coating system (primer + tie coat + top coat), or it can be temporary, such as a single coat of antifouling top coat. The intent of the permanent coating would be to provide biofouling mitigation, drag reduction, and optimize the hull potential [4] for the life of the propellers (or at least until the next docking work period); whereas, the intent of the temporary coating would be to provide biofouling mitigation until the ship is in active service. An optimal permanent coating system would be a foul release (FR) system, in which the top coat is a low surface energy coating that facilitates removal of biofouling. FR coatings do not contain a biocide, thus biofouling will occur; however, the biofouling adhesion is relatively low, and the growth is expected to slough off once the vessel is underway. Unlike ablative biocidal coatings, which must be replenished every few years, the FR coating is designed to maintain functionality for up to 10 years (depending on the product), barring mechanical damage. It is expected that the FR coating will sustain damage at the blade tips where cavitation is extremely high; however this is not a concern with respect to biofouling, as any growth will also be removed by the cavitation forces. An optimal temporary propeller coating to mitigate biofouling while the ship is alongside is a biocidal ablative antifouling coating. This type of coating will mitigate biofouling during the initial idle time, and slowly wear away when the ship becomes more active.

The aim of this investigation is to evaluate the impact of two different types of coatings, designed to address propeller biofouling, on the integrity of propeller material (NAB), under varying (full or no) cathodic protection (CP). The coatings chosen represent the two biofouling mitigation approaches outlined above—one is a marine epoxy coating that is the primer of the permanent coating system, and the other is a copper ablative antifouling that is the temporary biocidal coating. The evaluation comprised a periodic assessment of coated NAB specimens, immersed in low flowing natural seawater, and subjected to varying CP conditions. The periodic assessment was performed at 3, 6, 12, and 18 months of immersion, and involved photographing, as well sectioning the specimens for microscopic examination.

2 Experimental

Specimens of NAB, machined from an old propeller, were cut into small rectangular specimens, approximately 4" long x 1.5" wide x 1/8" thick. Elemental analysis of the cast NAB, determined by inductively coupled plasma – mass spectrometry (ICP-MS) as described below, identified the NAB to be UNS C95800: 9.6% aluminum, 4.9% nickel, 4.5% iron, 1.7% manganese, and the remainder copper.

2.1 ICP-MS Analysis of NAB

NAB samples were prepared for ICP-MS analysis using a closed-vessel microwave digestion method, in a 4:1 mixture of nitric acid and deionized water. The vessels were sealed and heated to 180°C as per method EPA 3052. ICP-MS analysis was performed using an Agilent Technologies 7500ce ICP-MS system.

2.2 SEM Imaging and SEM EDS Analysis

Backscatter electron images were collected on a Hitachi S-3700N scanning electron microscope (SEM). Elemental composition of the κ -phases, to assist in identification, were determined using Energy Dispersive X-Ray Spectroscopy (EDS). EDS spectra were collected using an Oxford X-Max Silicon Drift Detector (SDD) with a 20mm² window.

2.3 Optical Microscopy

Samples sectioned from the specimens were mounted in thermoplastic polymethylmethacrylate powder (epoxy samples) or cold mount epoxy (antifouling samples), and polished to 0.05 microns (μm) with alumina paste and cloth media. The samples were examined using an Olympus GX71 Inverted Metallurgical Microscope; the images were captured using Olympus Stream Motion software.

2.4 Silver Nitrate etch

To assist in the determination of regions subject to SPC, freshly polished metallographic specimens were etched with 10% silver nitrate (aq) for approximately 10 seconds, followed by wiping with a damp cotton ball. In areas of advanced SPC, where copper had been re-deposited, the etchant resulted in the deposition of silver onto re-deposited copper, yielding a dark region [5].

2.5 Specimen Preparation

For the antifouling experiments, four NAB specimens were abraded by hand with 400 grit emery paper. This was intended to roughen up the surface a bit for enhanced adhesion, but not significantly change the NAB surface profile. After an ethanol wipe, and allowing the surface to dry, the copper-ablative antifouling coating was applied by brush, in two coats, yielding a dry film thickness (DFT) of approximately 250 μm . The product applied contains up to 50% by weight copper (I) oxide, and up to 10% by weight copper (II) oxide.

For the epoxy experiments four NAB specimens were grit blasted to yield a surface profile of 50–75 μm . The more rigorous surface preparation was intended to ensure long term adhesion of the marine epoxy primer. After an ethanol wipe, and allowing the surface to dry, the epoxy primer was applied by brush, in two coats, yielding a dry film thickness of approximately 400 μm .

Once the coating had fully dried (antifouling) or cured (epoxy), an intentional breach in the coating was introduced by milling a lengthwise slot on each side of the specimen, completely through to the NAB surface. On one side, arbitrarily designated the front, the slot was two mm wide. On the back, the slot was five mm wide. Both front and back of each specimen was milled in order to allow for additional crevice locations; the slot widths were varied for differing exposed regions of NAB, to ascertain whether there was an effect. Figure 3 shows the front and back of the both sets of specimens after milling.

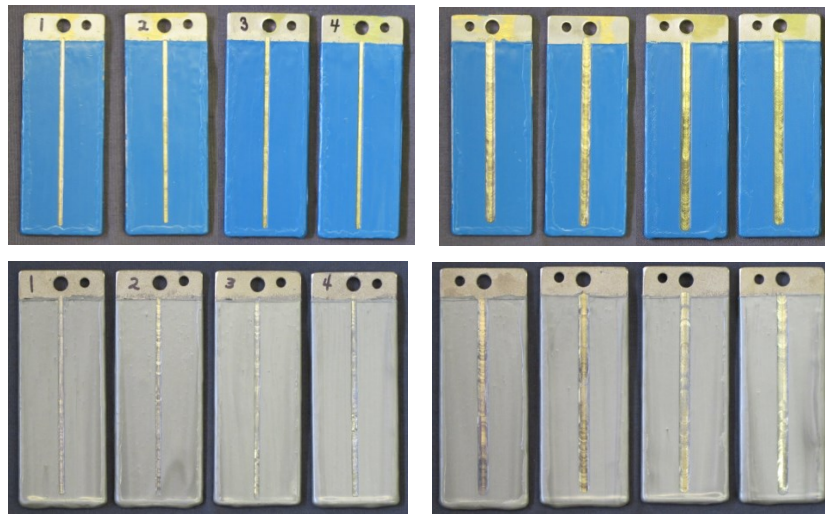


Figure 3: Front and back of antifouling-coated (top) and epoxy-coated (bottom) specimens after intentional defect had been milled on both sides: two mm on front, and five mm on back.

2.6 Experimental Set-Up

The two sets of experiments, each performed in duplicate, were set up in which one set was not cathodically protected (#1, #2) and the other set was cathodically protected (#3, #4). The cathodically protected specimens were each connected to a Gamry Reference 600 potentiostat, operated in potentiostatic mode (-850 mV vs. Ag/AgCl), with a graphite counter electrode, and a Ag/AgCl reference electrode. The specimens were immersed in a low flow seawater tank (Figure 4 and Figure 5), into which natural seawater was pumped from a small bay near Esquimalt Harbour, off the Strait of Juan de Fuca. For most of the experiment, the seawater within the system was flowing; however, for maintenance periods (approximately one week out of every month), the system was not flowing. During these periods, the seawater was aerated to ensure that the conditions were not completely stagnant.

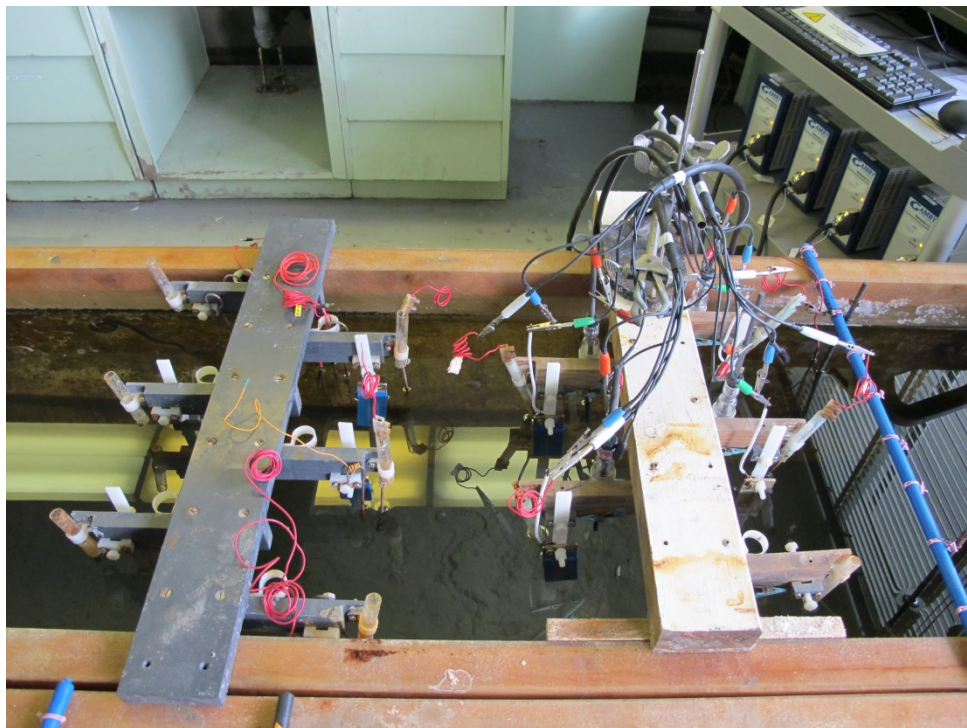


Figure 4: Experimental set up with specimens immersed in low flowing seawater tank. The specimens were oriented such that flow was parallel to the width of the specimen (flow across front and back were the same). Protected specimens were positioned downstream (right side) of unprotected specimens (left side) for proximity to the potentiostats.

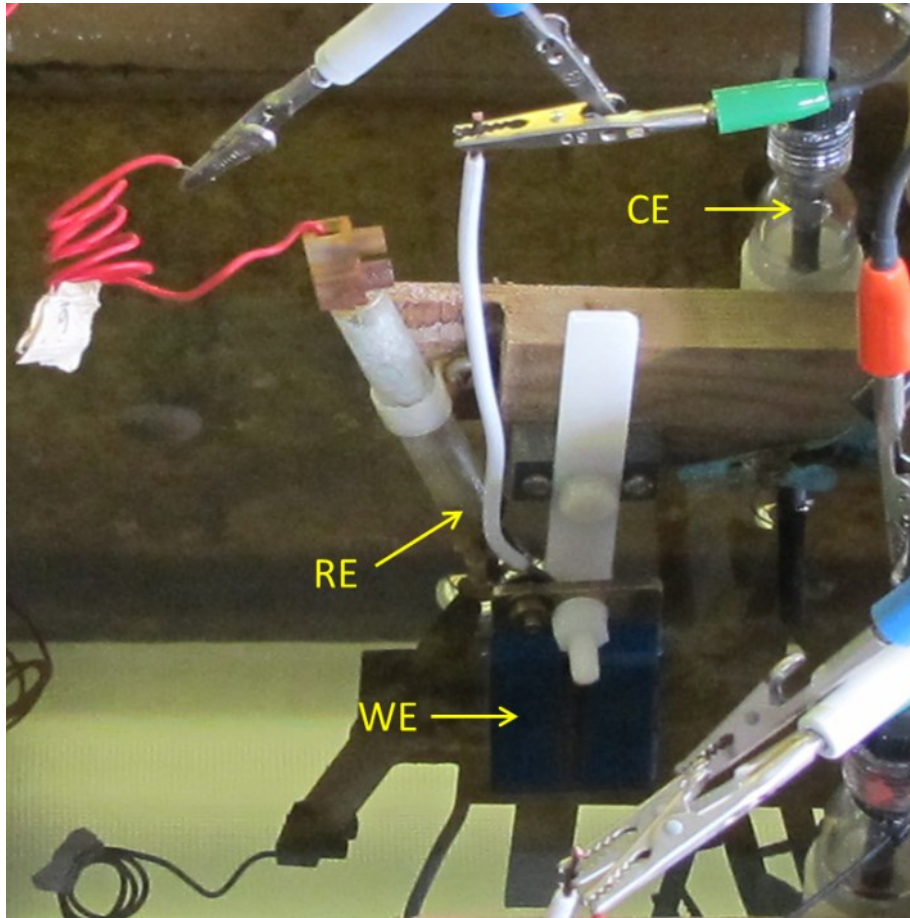


Figure 5: Close up of an immersed specimen, showing relative location of specimen (working electrode, WE), reference electrode (RE), and graphite counter electrode (CE).

The specimens were removed from the seawater at 3, 6, 12, and 18 months of immersion for visual examination as well as removal of a small cross-sectional piece from the bottom of each specimen. The cross-sectional piece was prepared for microscopic examination by mounting in either cold-cast epoxy (for antifouling specimens) or by hot press in poly(methyl methacrylate) (for epoxy specimens), and polished down to 0.05 μm alumina paste and cloth media. The cut edge of each parent specimen was repaired with epoxy coating and re-immersed in the seawater tank, except after 18 months, at which point the experiment was stopped.

3 Results and Discussion

The intent of this investigation was to evaluate the integrity of NAB in seawater under differing coating and cathodic protection conditions (fully protected or unprotected). Without cathodic protection, NAB will undergo selective phase corrosion, especially in crevices, due to the variation in potential of the different phases [1]. Crevices are created by anything that covers an area of the NAB, such as a coating or biofouling organisms. In these experiments, the applied coating functions as a crevice-former; however, the coatings utilized in these experiments exhibit different barrier properties. Part of this investigation was to assess the impact of their crevice-forming ability on the progression of selective phase corrosion (SPC).

3.1 Marine Epoxy

The epoxy experiments were intended to replicate conditions in which propellers may be permanently coated with a foul release system. Such a system typically employs an epoxy primer, chosen for its excellent adhesion and corrosion protection properties. In the full system, a tie coat would be applied to the primer to enhance adhesion with the foul release top coat, thus there are three products that comprise a full system. Since these experiments focus solely on the effect of the epoxy coating on NAB, the specimens were prepared with the primer only. The marine epoxy used in these experiments contains up to 10% aluminum flake, to enhance the barrier properties of the coating. The flakes tend to be oriented roughly parallel to the substrate surface, resulting in a tortuous path, thus slowing water ingress. In some locations, the flakes could be in contact with the substrate and therefore could provide some degree of cathodic protection by functioning as a sacrificial anode. However, this is not the primary purpose for their presence.

To adequately replicate propeller surface preparation, the NAB specimens were grit blasted, in order to achieve the desired surface profile of 50–75 μm . The grit-blasting, however, caused superficial mechanical damage (Figure 6), which could influence SPC.

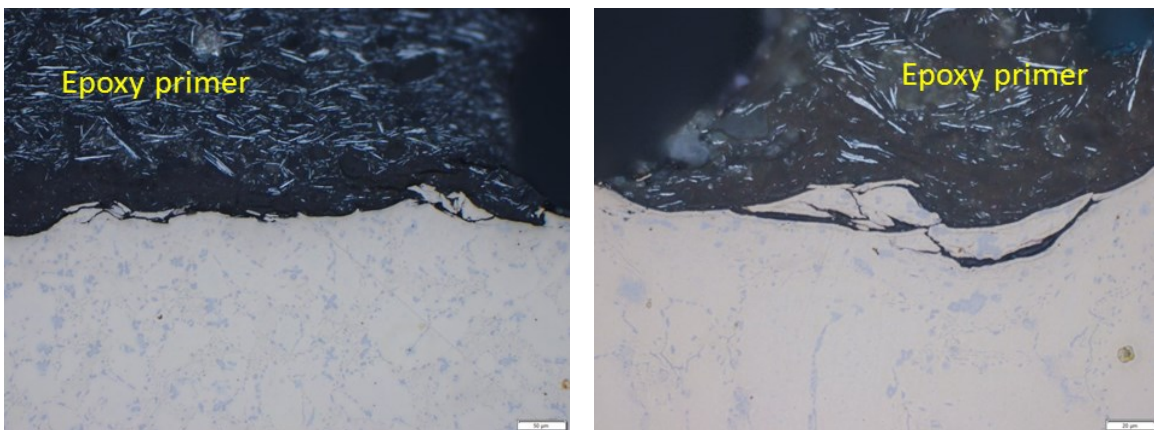


Figure 6: Mechanical damage noted on epoxy specimens, attributable to the grit blasting used to prepare the surface. Scale bars are 50 μm and 20 μm for left and right image, respectively.

3.2 Copper Ablative Antifouling

The antifouling experiments were designed to replicate conditions in which propellers are temporarily coated with an antifouling coating. The copper-ablative antifouling is a controlled depletion polymer containing a significant quantity of copper oxides (25–50% by weight copper (I) oxide and 1.0–10% copper (II) oxide) which function as the biocide. Seawater ingress results in dissolution of the copper oxide, causing slow release of copper ions from the surface of the coating. With time, the outermost region of the coating becomes depleted in biocide—this is known as the leached layer. While alongside, the leached layer increases in thickness, impeding the diffusion of biocide to the surface. However, the coating matrix is designed to ablate as the ship moves, essentially rejuvenating the coating, and allowing biocide release again. The coating matrix clearly does not function as a barrier coating. Indeed, it becomes thinner, and more porous over time, hence is not expected to function as a typical crevice former.

As use of the copper ablative is to temporarily mitigate biofouling, and is not intended for long-term use, coating adhesion is less important. Hence these specimens had minimal surface preparation (light sanding), ensuring a smooth surface and avoiding any mechanical damage to the NAB (Figure 7).

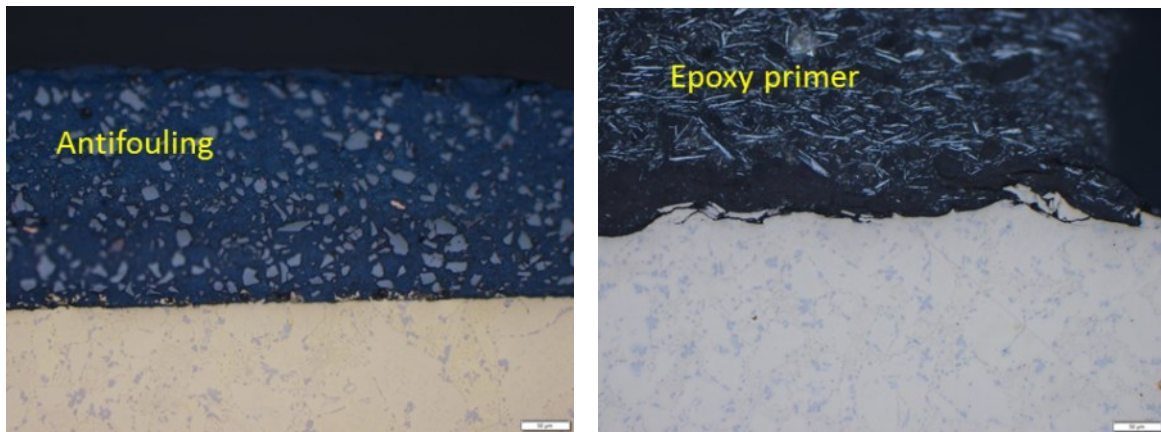


Figure 7: Note the smooth surface of the antifouling specimen (left), in contrast to the rough epoxy specimen (right) resulting from the grit blasting. Scale bars are 50 μm .

3.3 Unprotected Specimens

Photographs were taken of the specimens immediately after removal from the seawater after 3, 6, 12, and 18 months of immersion. Changes in the appearance of the exposed NAB, the presence of corrosion products, as well as any changes in the coating itself, were noted. In addition, pieces were sectioned from the bottom of each specimen, for microscopic examination; the parent specimens were repaired, and re-immersed.

Within 3 months of immersion, surface tarnishing (oxidation) of NAB and the formation of blue-green copper-based corrosion products were evident within the score line of the unprotected specimens (Figure 8). Red-brown deposits immediately adjacent to the coating were also noted. Although the formation of red-brown copper (I) oxide (Cu_2O) has been noted in previous studies [3], SEM-EDS analysis indicated that the red-brown corrosion product is primarily iron-based.

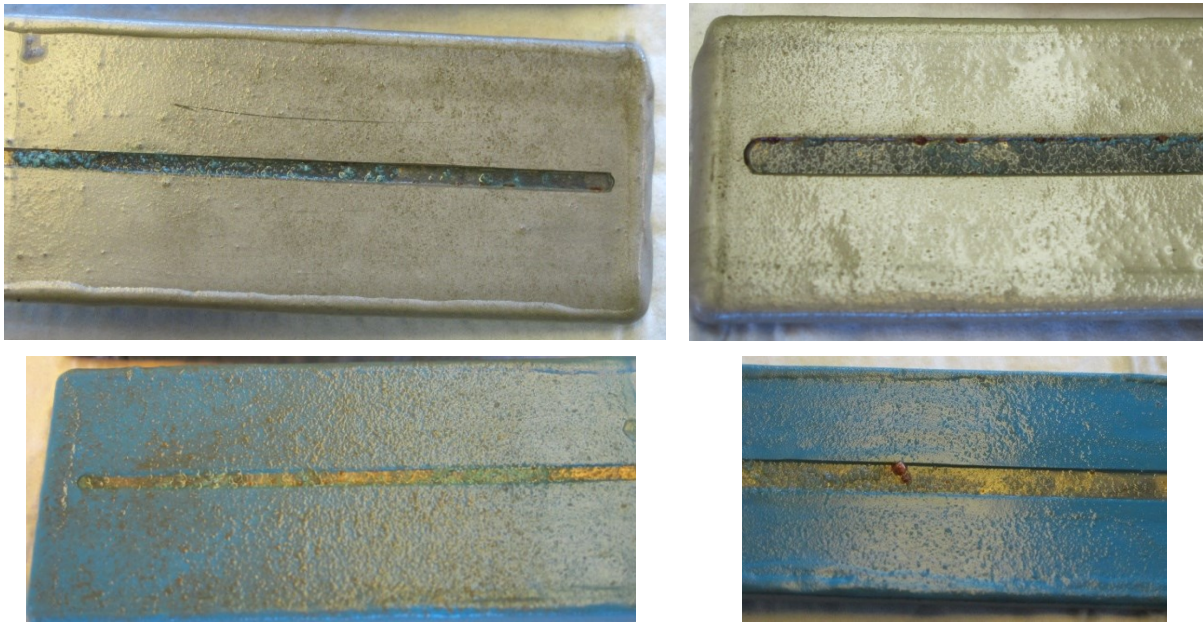


Figure 8: Unprotected epoxy (top) and antifouling (bottom) specimens exhibiting evidence of tarnishing as well as blue-green copper-based and red-brown iron-based corrosion products.

The exposed NAB in the score line was observed to darken with time. Figure 9 shows the specimens after 18 months of immersion. The epoxy specimens exhibited significant blistering adjacent to the crevice, and well under the coating, demonstrating considerable water ingress (Figure 10).

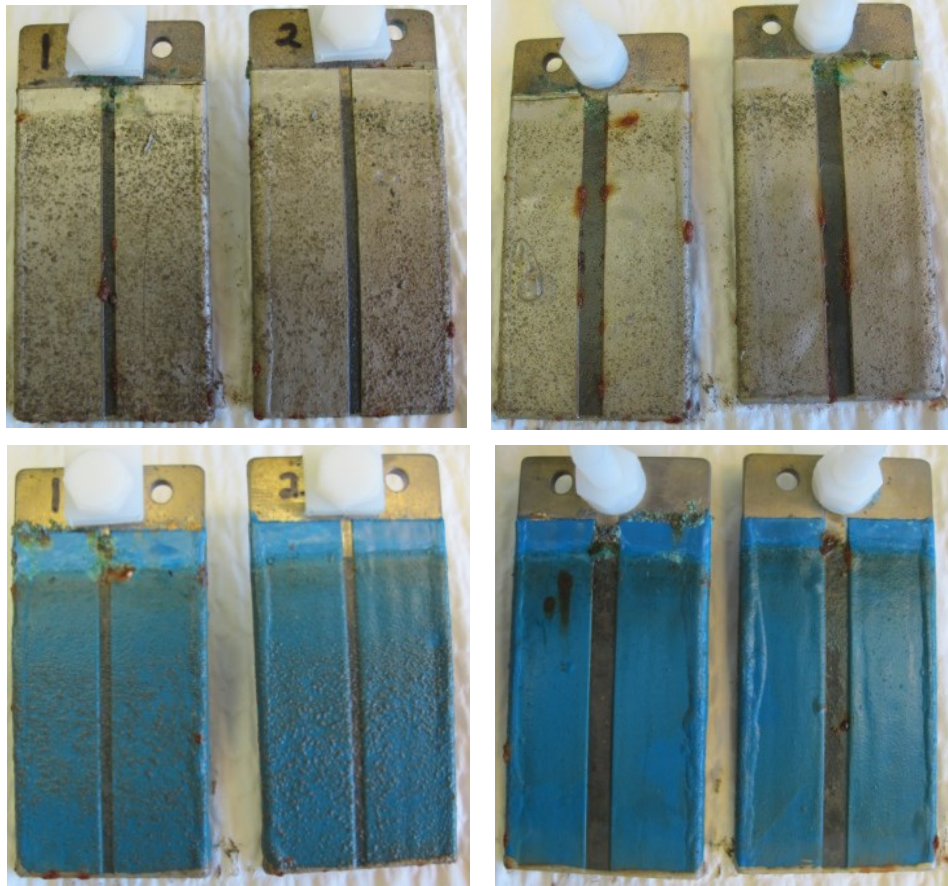


Figure 9: Front and back of unprotected epoxy (top) and antifouling (bottom) coated NAB specimens after 18 months.

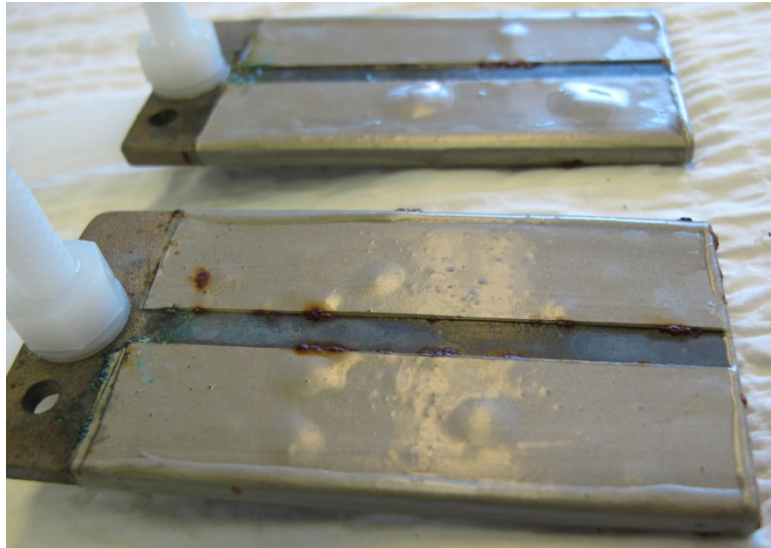


Figure 10: Unprotected epoxy specimens after 18 months of immersion, showing significant blistering at numerous locations.

Cross-sectional pieces were examined using optical microscopy. The specimens were scrutinized for any changes to the NAB, particularly the onset and progression of selective phase corrosion (SPC). Any changes to the coating were also noted. Due to the introduction of a score line on both sides of each specimen, the cross-section provides two independent score lines, and four potential crevice locations. The development of a crevice is expected to depend on the adhesion of the coating in that particular location.

In the absence of cathodic protection, SPC may occur in exposed areas of NAB, but particularly within crevices that may develop under the coating, as a result of poor coating adhesion. Initial crevice corrosion is expected to proceed with the oxidation of the α -phase, as it is more anodic than the κ -phases. As the SPC progresses, advanced crevice corrosion is expected to involve the oxidation of one or more κ -phases. The acidic environment within the crevice, along with depleted oxygen levels, causes destabilization of the protective oxide film of the κ -phase, rendering the κ -phase anodic to the α -phase [3]. Preferential corrosion of the κ -phase within the crevice ensues, as does the reduction of copper ions to metallic copper, resulting in copper re-deposition. The observation of re-deposited copper is evidence that crevice corrosion has advanced to the later stage, where the κ -phase(s) become anodic to the α -phase. The onset of κ -phase corrosion is dependent on the pH, the change in which is impacted by the diffusion of species into and out of the crevice. It is reasonable to expect that the diffusion rate will depend on the size, and perhaps geometry, of the crevice, thus it follows that crevice corrosion could progress at varying rates within the same specimen. For example, copper re-deposition may be observed in one area of a specimen much earlier than in another area.

At the 3 month examination, the epoxy specimens exhibited a small amount of early SPC (oxidation of the α -phase) within the score line, in addition to advanced SPC (i.e. copper re-deposition was evident) in one of four crevices, on each epoxy specimen (Figure 11). The antifouling specimens exhibited α -phase oxidation within the score line; however, no crevice corrosion was observed (Figure 11).

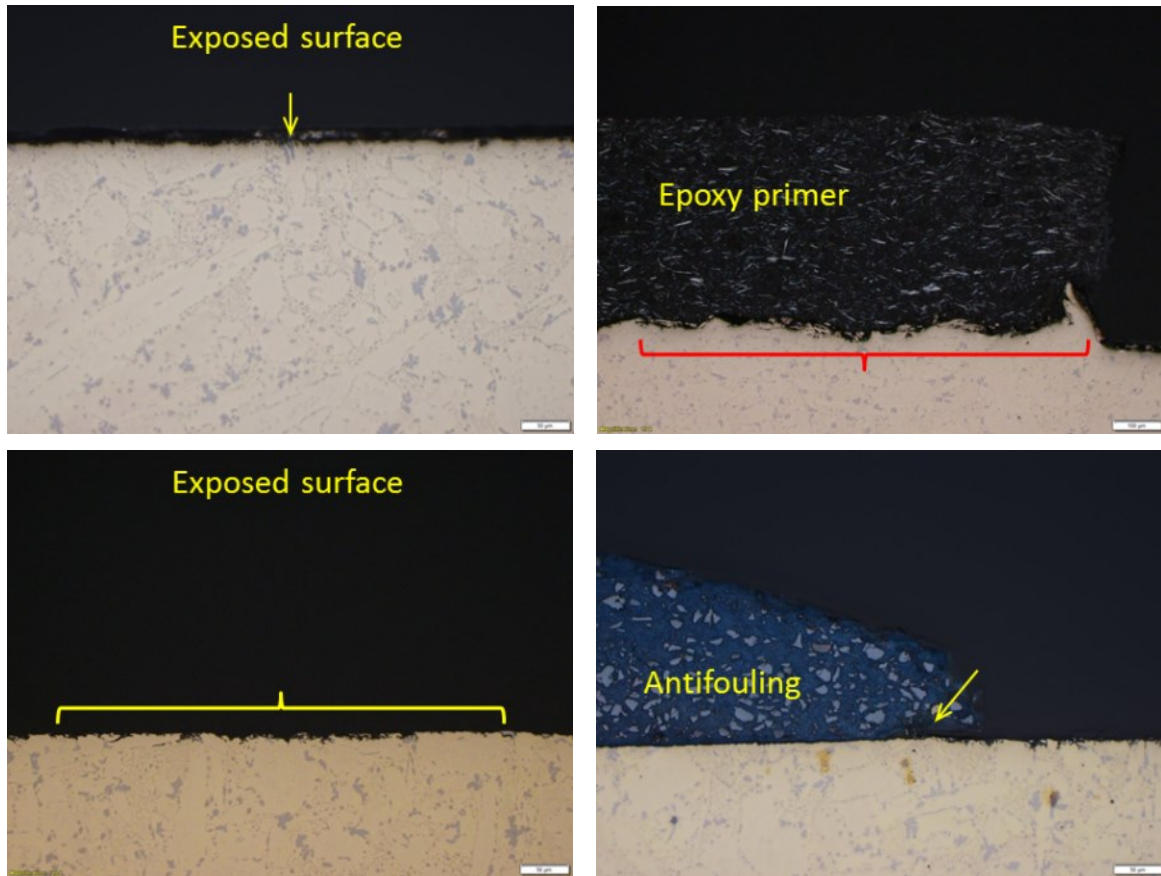


Figure 11: Images showing a small amount of SPC (just α -phase corrosion, yellow arrows and bracket) within the score line of epoxy (top left, scale bar 50 μm) and antifouling (bottom left, scale bar 50 μm). Advanced crevice corrosion (red bracket) was observed in the epoxy specimen (top right, scale bar 100 μm); however, very little crevice corrosion (α -phase) was observed in the antifouling specimen (bottom right, scale bar 50 μm).

The extent of crevice corrosion continued to increase with the epoxy specimens, however, the onset of crevice corrosion was significantly delayed with the antifouling specimens. There was no discernible crevice corrosion with the antifouling specimens until 18 months of immersion. Even at 18 months, crevice corrosion, noted in only two of eight crevices, was neither deep (less than 1 mm) nor advanced (no copper re-deposition).

In order to assess the extent of SPC on all unprotected epoxy specimens, freshly polished specimens were etched with silver nitrate solution to emphasize areas of SPC. This is a rough method for revealing SPC, although it is only effective if the SPC has advanced to the copper re-deposition stage. The silver, which oxidizes the re-deposited copper, is reduced and forms a dark deposit on the surface, rendering the SPC-affected areas more visible. To demonstrate the effect of the silver nitrate etchant, before and after images are presented in Figure 12. The areas that appear dark and “chewed up” were considered to be those with advanced SPC. The region exhibiting this effect continuously along the coating-NAB boundary was measured. In addition to the continuous areas of undercutting, some random dark spots at the coating-NAB boundary as well as within the bulk of the NAB were noted; thus it seems that some of

the κ -phases were also subject to oxidation. The silver nitrate etch should be considered a rough, but not definitive test for SPC. Dark spots that were noted along the boundary, but did not form part of the continuous area of effect were not included in the measurement; thus it is possible that the extent of SPC is greater than the values indicate.

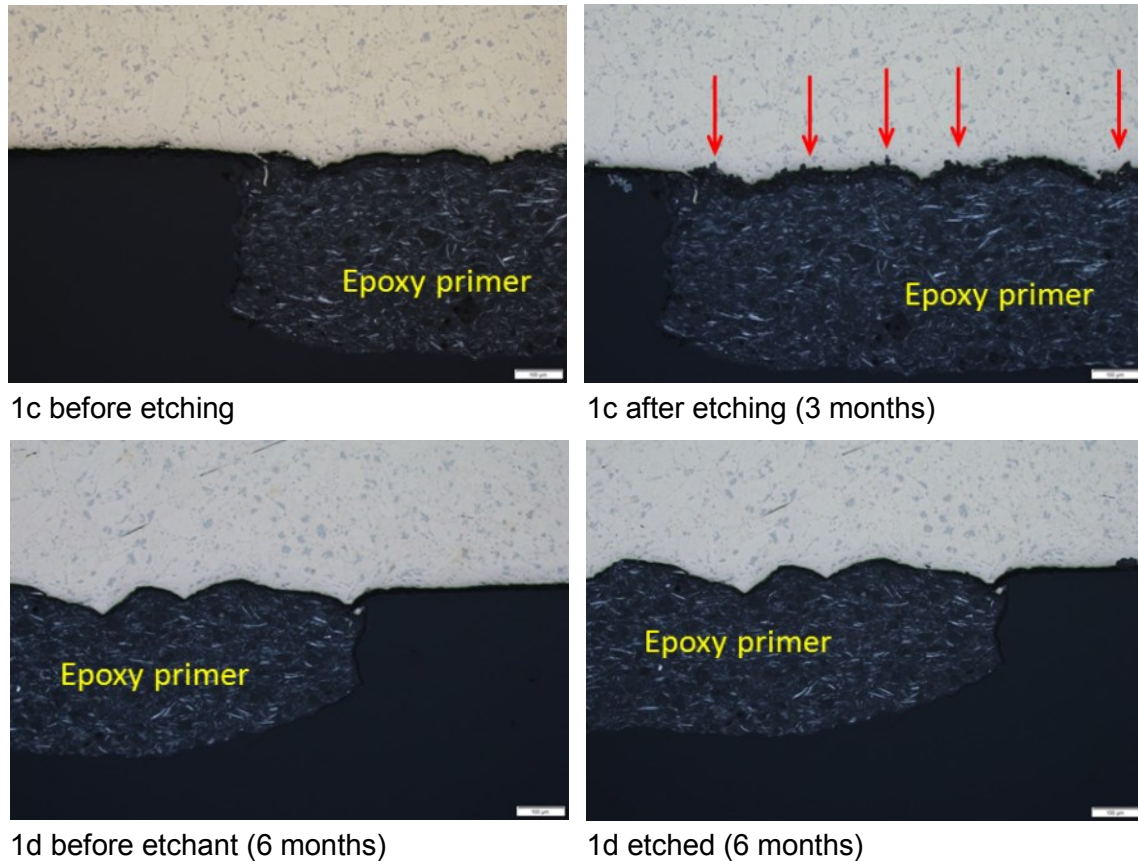


Figure 12: Images taken before and after etching demonstrate the effectiveness of using silver nitrate to better view advanced SPC. Until the SPC has progressed sufficiently for the re-deposited copper to be visible, it is very difficult to see the evidence of SPC on unetched samples. The top right image shows a distinct effect of the silver nitrate etch (red arrows), indicating advanced SPC; however, the lower images demonstrate no difference, before and after etching, indicating no advanced SPC. Scale bars are 50 μ m.

Crevice locations were defined relative to the thin and thick milled slots as shown in Figure 13. All four crevice locations on each unprotected epoxy-coated specimen were examined, and the extent of SPC under the coating was measured, in millimetres (mm) (Table 2).

In general, the extent of crevice corrosion increased with time (Table 2), both in number of affected crevices, as well as extent of undercutting in a given crevice. Although it is interesting to note that crevice corrosion developed at an inconsistent rate at the various crevice locations, even within the same sample. Specimen 1 showed a large variation in rate of undercutting progression, whereas specimen 2 exhibited crevice corrosion at only one location. This supports the notion that the geometry of the crevice impacts crevice corrosion. It is important to recall that these measurements were made on different samples cut

from the same specimen (at different times), hence the 6 month sample is not the 3 month sample at a later time, but is actually a different sample. This approach provides general trends, but variations in what appear to be the same crevice are not unexpected. The variation in slot width did not appear to impact the development of crevice corrosion.

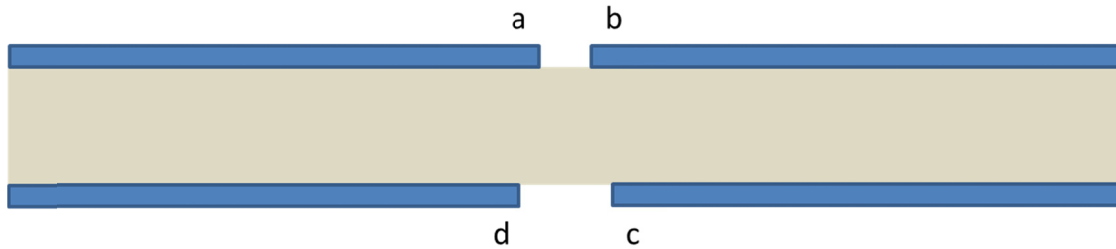


Figure 13: Diagram showing labelled crevices.

Table 2: Extent of Crevice Corrosion for Epoxy Specimens, by Crevice Location.

| Specimen | Measure of Undercutting (in mm) | | | |
|--|---------------------------------|---------------------|--------------------|------|
| | a | b | c | d |
| 3 month 300-1 | 0 | 0 | 2.5 | 0 |
| 6 month 300-1 | 5.3 | 0 | 7.3 | 0 |
| 12 month 300-1 | 6 | 11.5 | > 6.2 ¹ | 5.1 |
| 18 month 300-1 | 0 | > 12.1 ¹ | 5.7 | 14.8 |
| 3 month 300-2 | 0 | 0 | 2.75 | 0 |
| 6 month 300-2 | 0 | 0 | 6.8 | 0 |
| 12 month 300-2 | 0 | 0 | 10.9 | 0 |
| 18 month 300-2 | 0 | 0 | 13.5 ² | 0 |
| ¹ Beyond this depth, the coating was missing, thus undercutting extended farther than measured. | | | | |
| ² The specimen had been cut for mounting, and the undercutting was right to the edge, thus actually extended farther than measured. | | | | |

The silver nitrate etchant did not alter the appearance of the antifouling specimens (Figure 14), suggesting that the small amount of crevice corrosion observed had not yet progressed to the copper re-deposition stage. The significant degree of advanced SPC within approximately half of the epoxy specimens crevices, in contrast to the very slight early SPC crevice corrosion noted on one quarter of the antifouling specimens suggest that the epoxy coating is a much better crevice-former than the antifouling coating. The results are consistent with the epoxy exhibiting excellent properties, and strongly suggest that the in-service conditions should be carefully considered when selecting coatings for use on NAB.

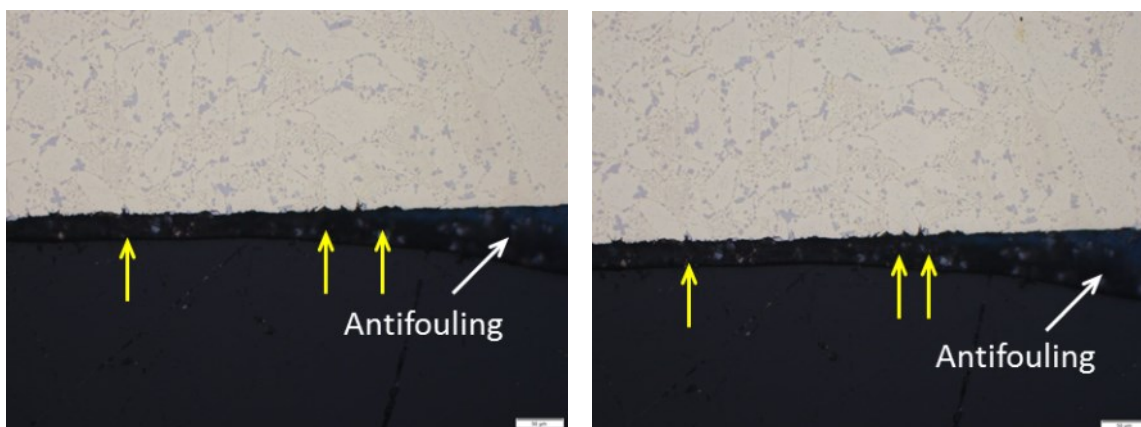


Figure 14: Images of crevice corrosion (early SPC) noted on an antifouling specimen after 18 months of immersion, before (left) and after (right) silver nitrate etch. The etchant does not indicate advanced SPC (copper re-deposition); however, early SPC is quite obvious. Scale bars are 50 μm .

3.4 Cathodically-Protected Specimens

Figure 15 shows the protected specimens after 18 months of immersion. For the most part, the protected epoxy specimens retained the shiny appearance of exposed NAB, consistent with unoxidized NAB, over the 18 months of immersion. In contrast, the protected antifouling specimens exhibited darkening at exposed NAB, which became progressively darker with time. Considering that the specimens had been subjected to the same conditions,³ it is reasonable to conclude that the observed differences in their appearance must be attributed to differences in the coatings. A viable explanation of the NAB darkening with the antifouling specimens is that the leached biocidal copper ions undergo electrodeposition onto the exposed NAB regions. This phenomenon has been observed previously⁴ when antifouling-coated NAB was immersed in a large beaker of seawater and cathodically protected; copper was observed on the surface of the NAB, and did not arise from SPC.

Although the protected specimens did not exhibit evidence of crevice corrosion, the surface of the epoxy-coated NAB appears to have suffered some degradation. In comparison with the mechanical damage attributed to grit-blasting (Figure 6), the damage seems to be more extensive and on a smaller scale (Figure 16). The NAB surface seems less well-defined, with several small cracks visible. The silver nitrate test did not modify the appearance, ruling out advanced SPC; however, early SPC should not be precluded. Unfortunately these experiments could not be continued⁵ as monitoring further development of the damage would have allowed a definitive assessment of the effect of grit-blasting on the integrity of NAB.

³ These conditions included power outages, in which the specimens were not cathodically protected, as well as possible excursions in applied potential. The total time in which the specimens were not cathodically protected was approximately six days.

⁴ Unpublished results.

⁵ The closure of the facility in which these experiments were underway necessitated the early conclusion of these experiments.

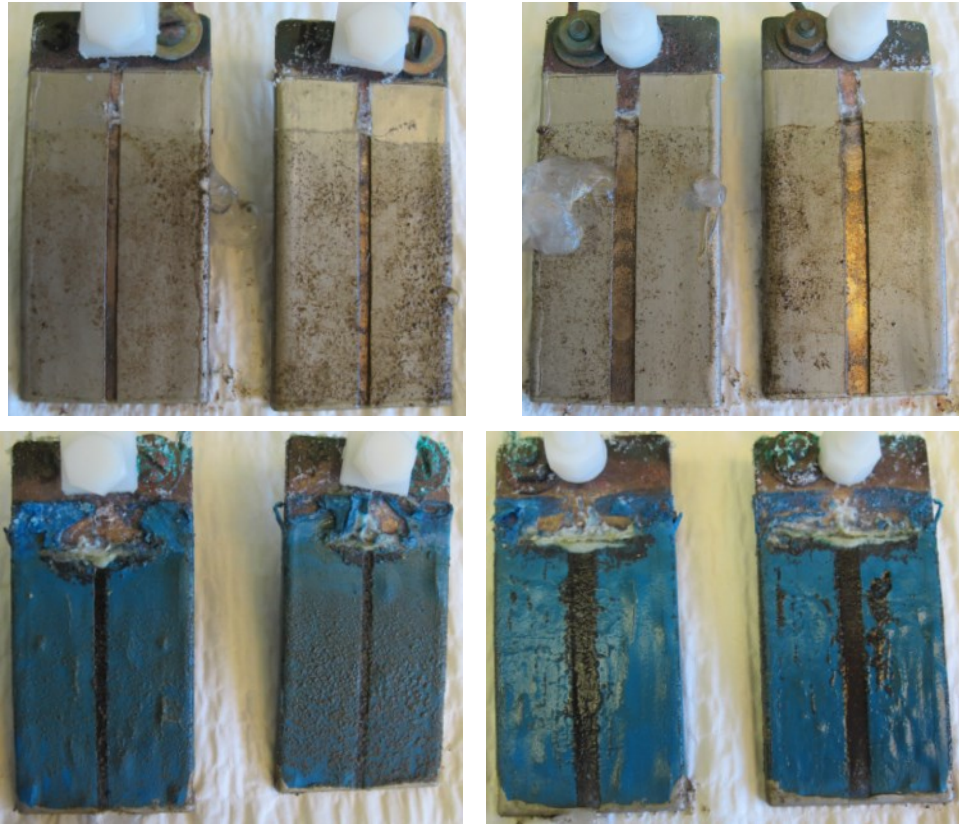


Figure 15: Front and back of cathodically-protected epoxy (top) and antifouling (bottom) specimens after 18 months.

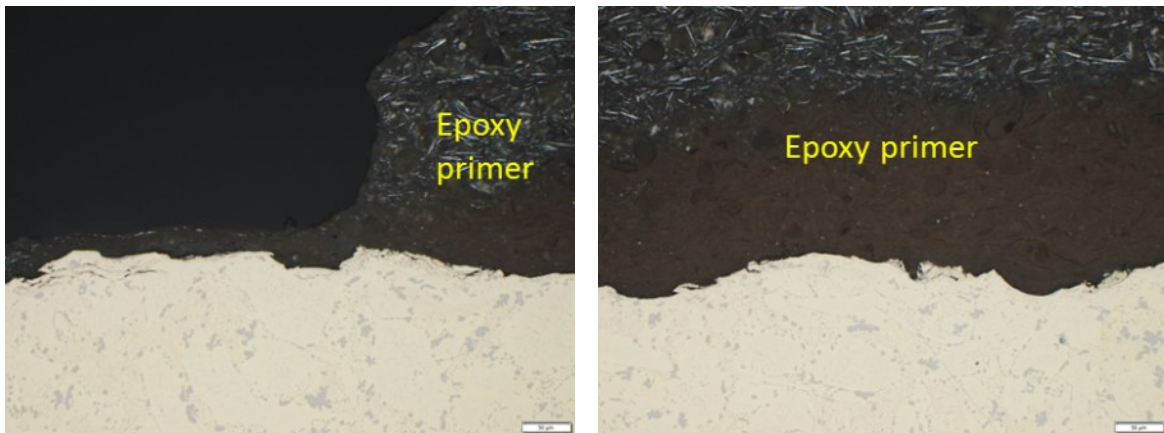


Figure 16: Protected epoxy after 18 months of immersion. Note the presence of micro-cracks near the surface, in contrast to the larger scale damage noted after grit blasting (see Figure 6). Scale bars are 50 μm .

Attempts to determine whether SPC is occurring deep within a crevice, where the cathodic protection may not be adequate⁶, involved the use of the silver nitrate test. The application of the etchant on epoxy specimens, after 18 months of immersion, did not result in any change in appearance (Figure 17). Although this likely means that SPC has not occurred, it does not preclude the existence of early SPC, as the silver nitrate provides indication of advanced SPC, as noted with the unprotected antifouling specimens discussed earlier (see Figure 14).

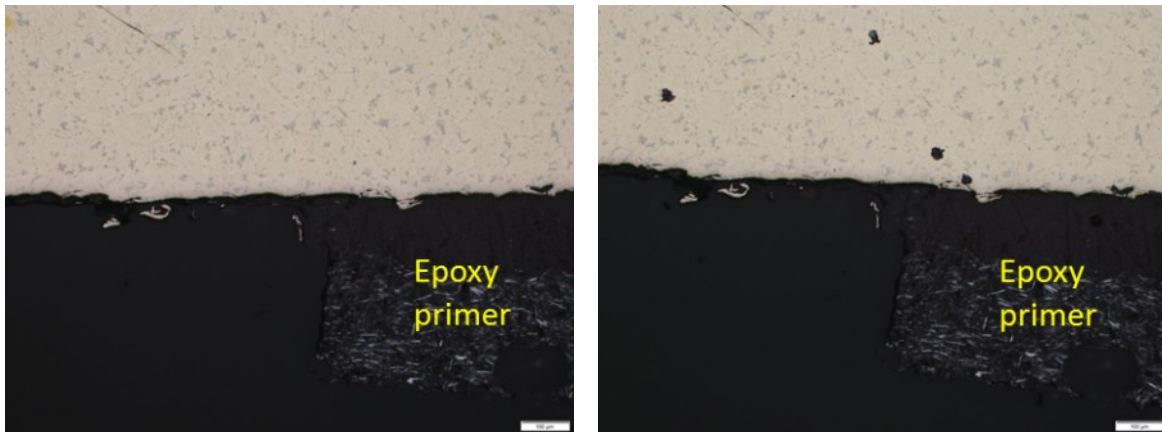


Figure 17: Protected epoxy after 18 months before (left) and after (right) silver nitrate etchant, showing no evidence of advanced SPC. Scale bars are 50 μ m.

3.5 Copper Conversion and Electrodeposition

Under conditions of cathodic protection, copper oxide in electrical contact with the substrate can be reduced to metallic copper. This process is known as copper conversion and was first noted on ships' hulls in the 1960's [6]. Copper conversion can arise when the copper oxide-containing antifouling coating is not electrically isolated from the cathodically protected hull, such as when the primer is too thin or contains voids, or when the antifouling is applied directly to the cathodically protected substrate.

This phenomenon was noted in these experiments as early as the 3 month mark, and the degree of copper conversion was found to roughly increase as a function of time (Figure 18). These regions are either adjacent to the score line, or at the edge of the specimen where the coating is thinner.

In addition to copper conversion within the coating, reduction of the leached biocidal copper ions onto the surface (electrodeposition) can also occur. This phenomenon was noted on protected antifouling specimens after 18 months of immersion (Figure 19). This process clearly modifies the surface of the substrate, and is likely detrimental to a propeller surface, as it could impact drag and noise.

⁶ Cursory modelling performed at Defence Science and Technology Group (DSTG), Australia indicates that the polarization (to protective potential) diminishes within a crevice relatively close to the mouth of the crevice. More rigorous studies are underway.

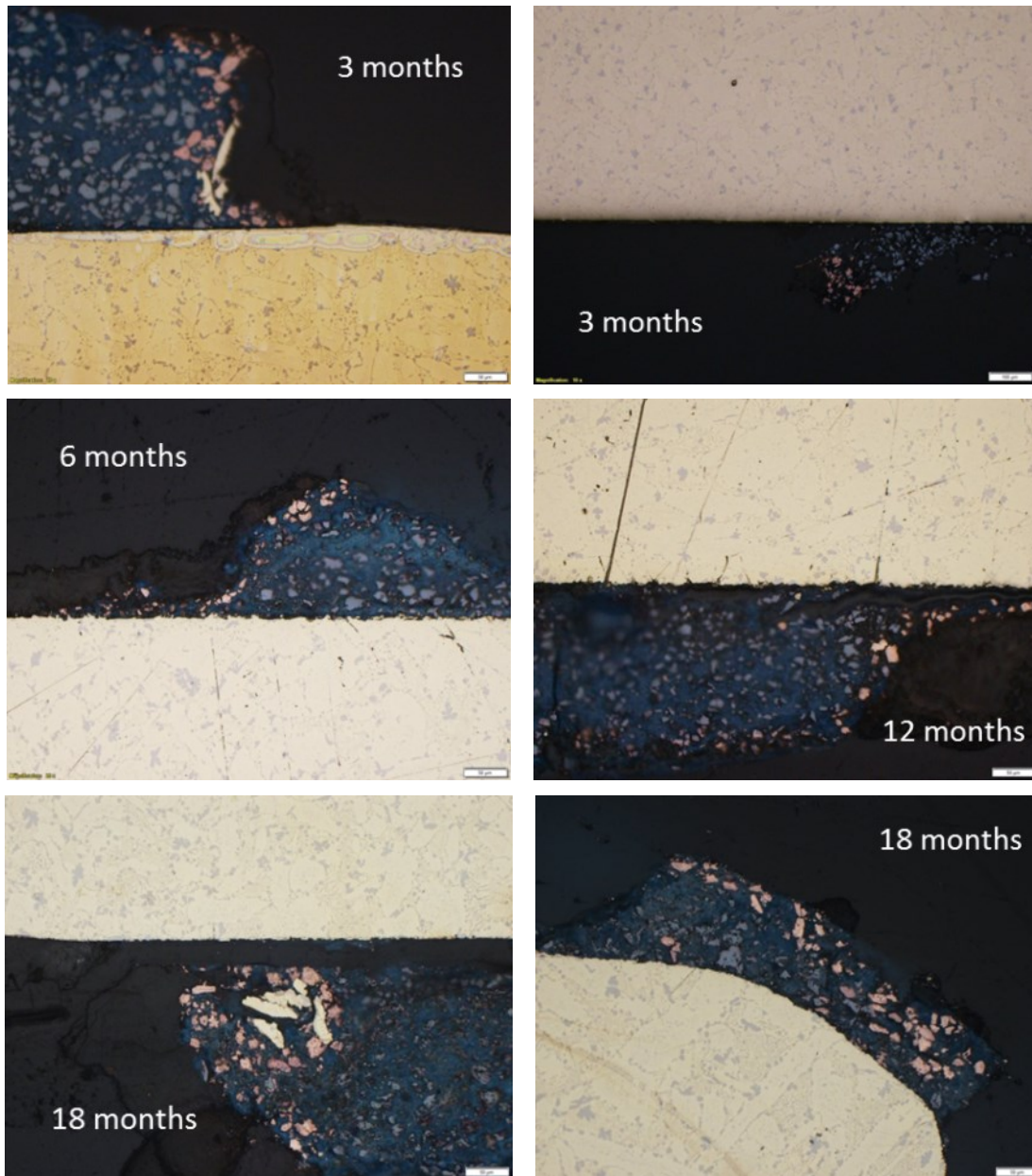


Figure 18: Images of protected antifouling-coated specimens showing evidence of copper conversion as early as 3 months, and roughly increasing in degree as a function of time (top—3 months, middle—6 and 12 months, lower—18 months). Copper conversion refers to the process by which the copper oxide particles in the antifouling coating undergo reduction to metallic copper, as a result of the cathodic protection current. Areas most susceptible to copper conversion are areas where the coating is very thin, such as at corners (lower right), are areas adjacent to a breach in the coating (all other images). Scale bars are 50 μm .

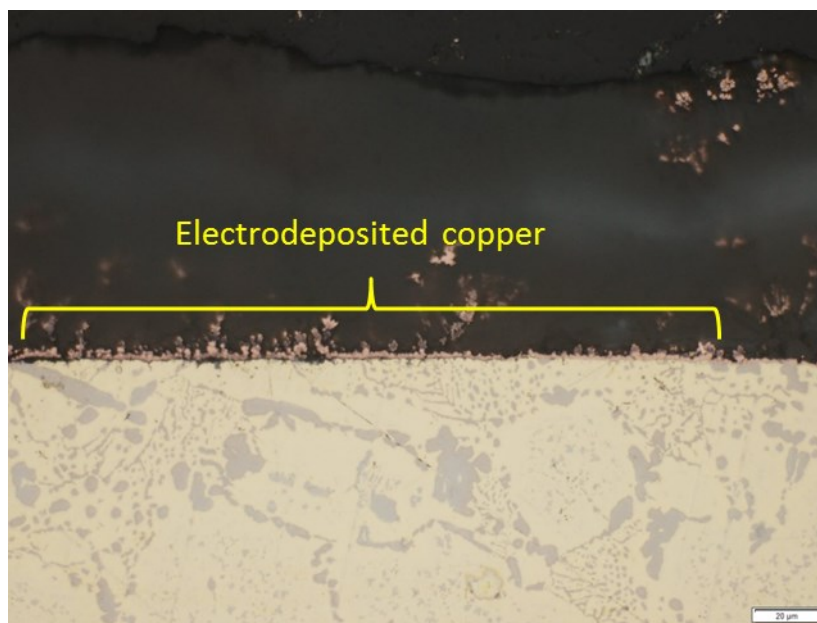


Figure 19: Copper deposition visible on exposed area of NAB after 18 months of immersion. Scale bar is 20 μm .

4 Conclusions

The crevice corrosion behavior of unprotected NAB was found to depend heavily on the nature of the coating. Not surprisingly, an excellent barrier coating (marine epoxy) functioned as a significant crevice-former, whereas the ablative antifouling coating did not. In the absence of cathodic protection, crevice corrosion under epoxy can be quite extensive, once initiated. The antifouling coating is a better NAB treatment to mitigate biofouling, although SPC, including a small degree of crevice corrosion, will occur.

With the cathodically protected specimens, the integrity of NAB appeared to be maintained with the epoxy system, for the duration of the experiment. In the event that epoxy is to be applied to NAB, it is critical that cathodic protection be adequately maintained. The effect of the grit-blasting on the mechanical integrity of NAB, in conjunction with the possible limitation of cathodic protection deep within a crevice, could result in long-term issues. It is highly recommended that long term (minimum five years) experiments be performed to fully gauge the impact of the presence of coating on the integrity of cathodically—protected NAB.

The copper ablative antifouling coating, however, was found to result in the undesirable electrodeposition of copper onto the surface of the NAB, increasing its roughness, and could potentially cause issues with drag and noise. This method could be a viable means of mitigating biofouling for a short period (less than 12 months); however, long-term use of antifouling on cathodically protected NAB is not recommended, due to the possibility of electrodeposition of copper onto NAB.

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List of symbols/abbreviations/acronyms/initialisms

| | |
|-------------------|--|
| Ag | silver |
| AgCl | silver chloride |
| AgNO ₃ | silver nitrate |
| Al | aluminum |
| CE | counter electrode |
| CP | cathodic protection |
| Cu | copper |
| DLP | Dockyard Laboratory Pacific |
| DND | Department of National Defence |
| DRDC | Defence Research and Development Canada |
| DSTG | Defence Science and Technology Group |
| EDS | Energy Dispersive X-Ray Spectroscopy |
| EPA | Environmental Protection Agency |
| Fe | iron |
| FR | foul release |
| ICCP | impressed current cathodic protection |
| ICP-MS | inductively coupled plasma – mass spectrometry |
| µm | micrometre |
| mm | millimetre |
| Mn | manganese |
| mV | millivolt |
| NAB | nickel aluminum bronze |
| Ni | nickel |
| RE | reference electrode |
| SDD | Silicon Drift Detector |
| SEM | scanning electron microscope |
| SPC | selective phase corrosion |
| UNS | Unified Numbering System |
| vs | versus |
| WE | working electrode |

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| 5. DATE OF PUBLICATION (Month and year of publication of document.) August 2018 | 6a. NO. OF PAGES (Total containing information, including Annexes, Appendices, etc.) 32 | 6b. NO. OF REFS (Total cited in document.) 6 |
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To investigate coatings-based methods for propeller biofouling mitigation, specimens of nickel aluminum bronze (NAB) were prepared by coating with either marine epoxy or copper ablative antifouling, and scored on each side, to expose the NAB. The specimens were immersed for 18 months in low flowing seawater, under either full or no cathodic protection. The specimens were assessed at 3, 6, 12, and 18 months; the assessment included the removal of a small cross section for microscopic examination. The integrity of the NAB at the crevices, due to the score lines, was monitored as a function of time. The coating condition was also monitored; the onset of copper conversion was noted by the 3 month mark with the protected antifouling coated specimens, and continued to increase with time. Furthermore, the electrodeposition of copper onto exposed NAB was also noted with protected antifouling specimens.

Dans le but d'étudier les procédés de revêtement pour atténuer l'encrassement biologique des hélices, on a préparé des échantillons de bronze au nickel-aluminium (BNA) en appliquant une couche antisalissure ablative à base de cuivre ou d'époxy marin. Les échantillons ont été entaillés de chaque côté afin d'exposer le BNA. On les a ensuite immergés pendant dix-huit mois dans de l'eau de mer à faible débit, avec ou sans protection cathodique complète, puis vérifiés après trois, six, douze et dix-huit mois, notamment en procédant à une petite coupe transversale afin de les examiner au microscope. L'intégrité du BNA, à l'emplacement des entailles, a été vérifiée en fonction du temps. On a également vérifié l'état des revêtements et constaté qu'une transformation du cuivre s'était amorcée après trois mois chez les échantillons protégés par un revêtement antisalissure et que celle-ci avait progressé au fil du temps. De plus, on a constaté l'électrodéposition du cuivre sur le BNA exposé chez les échantillons avec protection antisalissure.

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selective phase corrosion; nickel aluminum bronze; antifouling coating; epoxy coating; copper conversion