Low-pressure cold metal spray coatings for repair and protection of marine components

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Synopsis

The marine environment is hostile to most engineering materials, a combination of in-service wear and exposure to marine environment leads to an accelerated material degradation. Insufficient or poor protection of the substrates further assists the accelerated material degradation in marine environment.

There is a direct relationship between the material-state of a ship and its operational capability, readiness, and service life. The current state-of-the-art practice is to use paint-based coatings to maintain the material-state of ships. However, the protection offered by paint coatings is usually brief due to inherent permeability and low damage tolerance of these coatings. For this reason, the paint coatings require renewal at regular intervals, typically less than 5-years, to maintain a minimum level of protection from the marine environment. The need for regular painting of ships results in a significant negative impact on the through-life availability, operational capability/readiness, and the cost of maintenance/operation of naval ships. Therefore, the fleet owners and operators should look beyond the conventional paint-based coatings to achieve significant breakthrough improvements in maintaining and enhancing the material-state of naval ships.

Metallic coatings, if selected and applied appropriately, will outperform the paint coatings in the marine environment. Historically, the cost and performance of metallic coatings, mainly thermal metal spray (TMS) coatings, prevented their widespread use in the marine industry. The TMS coatings also have their own inherent application and performance related limitations that are widely reported in the literature. However, the cold metal spray (CMS) coating process can overcome the application and performance related limitations that are typically associated with the TMS coatings, therefore creating an opportunity for widespread use of metallic coatings in shipbuilding and fleet upkeep/maintenance.

In this paper, the ability of low-pressure (LP-CMS) coatings to repair and reclaim damaged marine components, and application of functional coatings to improve in-service damage tolerance of the damaged/new components is investigated. The results of the investigation show that two LP-CMS coatings, Al-alloy and CuZn-alloy, can be used to repair and preserve both new and damaged components. The accelerated salt-spray and natural immersion corrosion testing of the LP-CMS coatings showed that each coating will be better suited to a particular operational environment, i.e. CuZn-alloy coating performed well in both immersion and atmospheric corrosion environments, whereas Al-alloy coating performed well only in atmospheric corrosion environment.

Keywords: Corrosion; Functional Coatings; Low-Pressure Cold Metal Spray; Damage Tolerance, Naval Ships, Repair and Reclamation

1. Introduction

Traditionally, a time-dependent, periodic, preventive-corrective, maintenance schedule is employed for naval ships (Ford et al, 2015). The length of a typical maintenance period can range from a few weeks, to months, and even years, depending on the extent of the work needed to restore the seaworthy material-state of the ships.

Since early 1990s, there has been a gradual decline in the number of operational warships in the Royal Navy (RN) surface fleet (Defence Select Committee, 2016). However, considering the current developments in the foreign naval capabilities, the deployments and workload of the RN will continue to increase in the years and decades to come. Combining this scenario with the ever-increasing pressure of ongoing budgetary cuts means that the fleet maintainers must look into cost efficient ways to improve the availability and reliability of RN warships to meet current and future operational demands of the RN. The technologies that can facilitate improved material-state of naval ships will be of interest to the fleet owners, operators, and maintainers alike.

To assist this cause, the latest developments in the enabling technologies such as the latest 'surface engineering' techniques can be investigated to enhance the material-state of naval ships.

Surface engineering is the practice of modifying the mechanical, chemical, and topological properties of a material to enable reliable and durable service in a particular operational environment. Surface engineering is a growing area of research as it offers an immense potential to improve the reliability and durability of engineering components operating in harsh environments. Some typical examples of surface engineering in use in the marine and adjacent industries are listed below:

- Application of anti-skid aero-thermal resistant thermal metal sprayed Al-Al/Ti coating on aircraft carrier flight deck for resilient operation under short take-off and vertical landing jet-efflux environment (Duthie, 2016);
- Application of thermal and cold metal spray coatings for wear and corrosion protection of components used in naval ships, such as main propulsion shaft of mine countermeasure ships, pump components, ball and globe valves (Kim et al, 2011).

The failure of a component begins when the material is unable to withstand the forces and/or the environment that it has been exposed to in-service. The selection of a suitable material with appropriate material properties, especially the surface properties, is crucial to achieve a reliable and durable performance in-service. However, it is often impractical, inefficient, and uneconomical to manufacture the components from the bulk material merely to achieve the desirable surface properties. An example of this is the use of titanium in marine applications. Titanium has a naturally occurring titanium-oxide (TiO_2) passive-film on its surface, which protects it from the harsh marine environment. However, titanium is roughly an order of magnitude more expensive than the carbon-steel without considering the cost of machining which is immensely expensive for a tough material like titanium. A better alternative in this case will be to use an inexpensive, readily available, and easily machinable material, such as steel or aluminium to manufacture the component, and then infuse the suitable surface properties by using an appropriate surface engineering process. The use of 'functional coatings' is the best way to surface engineer an inexpensive and readily available material such as carbon steel or aluminium. The use of functional paint coatings to protect the steel substrate from the marine environment is a good example of surface engineering. However, the problem with the paint-based coatings is that they do not last long in the marine environment due to their inherent heterogeneity, permeability, and poor damage tolerance (Lyon et al, 2017).

A relatively new metal coating technique 'Low Pressure Cold Metal Spray (LP-CMS)' offers a novel way to apply the functional metal-matrix composite coatings to a range of different types of substrates, including - metals, alloys, plastics, composites and concrete. Additionally, the LP-CMS process can be used to customise the material properties of a coating to suit an intended operational environment, for example – varying the composition of a coating to increase damage tolerance to erosion, corrosion or fatigue. The LP-CMS technique can also be used to conduct repair and restoration of any non-structural damage in the operational components. The US Army Research Laboratory (ARL) pioneered the use of CMS coatings to repair and restore high value and obsolete hard to source components, such as repair of chafing damage in riveted aircraft skin panels, dimensional restoration of erosion damage in UH-60 black Hawk gearbox sump magnesium housing, F-18 aluminium housing, F-16 air inlet housing. They even have a military standard (MIL-STD-3021) for the manufacturing control of cold spray coating processes.

2. A summary of the typical material degradation mechanisms in marine environment

The harsh marine environment can cause a number of different types of material degradation mechanisms to a component such as various forms of corrosion, erosion, biofouling, and a combination of these. Most material degradation mechanisms are complex in nature due to a naturally occurring synergy between the material degradation mechanisms (discussed below) and the operational environment.

2.1. *Corrosion*

Corrosion is the natural degradation of a material due to electrochemical reaction. There are many forms of corrosion, but they all depend on the presence of an electrochemical cell to initiate corrosion reactions. The electrochemical cell is usually a result of change in chemical, physical, or mechanical properties of a material, or environment (electrolyte). Mainly three types of electrochemical cells are responsible for all forms of corrosion in the marine environment (Revie and Uhlig, 2008):

- Galvanic cell - also known as active-passive differential cell corrosion, occurs when two materials with vastly different electro-potentials are brought into contact with each other either physically or with a conductive electrolyte.

- Concentration cell - when potential difference required to initiate corrosion reactions is driven by the vastly different concentrations of salt ions and/or dissolved oxygen in the electrolyte.
- Differential temperature cell - when a material is exposed to the temperature gradient that exists either within the material or in the electrolyte.

2.2.   Erosion

Erosion is the wear of a material caused by a concentrated and repeated mechanical and/or electrical attack on the material surface. The loss of material is caused by a localised decay in the mechanical and thermal properties of the material (Wood, 2006). There are mainly three types of erosion mechanisms:

- Abrasive erosion - caused by repeated impacts of solid particles in a stream of gas or liquid. The impinging particles are usually harder than the substrate material.
- Cavitation erosion - caused by the impingements of high velocity micro-jet and cyclic shock waves resulting from the cavitating bubbles. The energy released from the imploding bubbles at or close to the material surface causes the damage similar to micro-fatigue.
- Electro-erosion -caused by the sparking discharge resulting from the stray current that has been released from the wrongly set on-board and/or shore side impressed current cathodic protection systems, or ineffective earthing of rotating machinery.

2.3.   Biofouling

Most materials exposed to the seawater are susceptible to biofouling. There are two types of biofouling:

- Micro-fouling - formation and adhesion of a slimy biofilm from the organisms such as bacteria and diatoms.
- Macro-fouling - attachment of larger, distinct multicellular organisms visible to the naked eye such as barnacles, tubeworms, molluscs, and fronds of algae.

Biofouling can influence the corrosion of a material by changing electrochemical conditions at the substrate-solution interface. The settlement of biofouling and microorganisms on the material surface will alter its local environment in terms of pH, dissolved oxygen, concentrations of organic and inorganic species. This will stimulate a localised corrosion cell, which will then create the conditions where microbial species will flourish further, thus resulting in an accelerated microbial induced corrosion (MIC) (Little and Lee, 2007).

As discussed previously, the most devastating form of materials degradation in marine environment result from a synergy between the above mentioned material degradation mechanisms. An example of this synergy is the accelerated erosion-corrosion damage of seawater system components such as valves, pumps, pipework and condensers, and underwater propulsion and control components. The extent of accelerated erosion-corrosion damage is evident in the pictures of the Port and Starboard rudders of HMS Al-Shamikh corvette shown in Figure 1. The damage was accrued after just 40 hours of operation above 20 knots (Webb, 2017). A combination of the propeller tip vortex and the rudder sheet cavitation caused the erosion of the inboard surfaces of the Port and Starboard rudders. The exposure of a freshly eroded surface to the seawater will result in severe corrosion attack that will further weaken the material surface for additional erosion attack - this will cause a vicious cycle of erosion-corrosion synergy resulting in extensive damage of the rudder material.
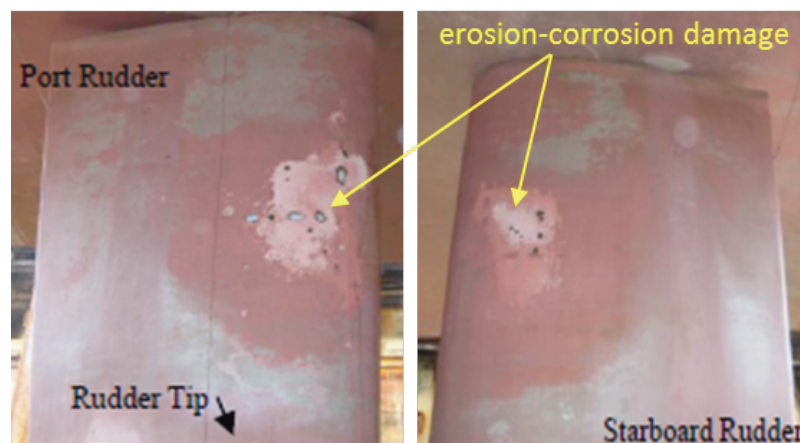

Figure 1: Synergistic erosion-corrosion damage of corvette rudders (Webb, 2017)

3. Surface engineering and the LP-CMS coating technique

The LP-CMS technique is an ideal process for depositing metallic coatings during construction and upkeep of ships for the following reasons:

- It is portable, the equipment footprint is <2ft^2, weighs <20 kg, and needs only standard 6.2 bar compressed air and 220 VAC (3.3 kW) mains electricity for operation.
- The functional properties of the coatings deposited with LP-CMS process can be tailored by varying the composition of the feedstock powder, or by applying and grading the multiple layers a coating with different material compositions and/or process parameters.
- The LP-CMS coating technique requires no exclusive health & safety administration, such as hot-permit, removal of insulation/flammable material from behind the substrate, combustible gases or fuels, and enclosed or restricted spaces for the coating deposition operation.
- The LP-CMS coatings are deposited at low temperatures so there is no risk of material oxidation resulting in superior mechanical and material properties.
- The consistency and repeatability of the coating process is good.
- The cost of operation and coating deposition is comparatively low.

The limitations of LP-CMS coating process are that it is a line-of-sight process and requires a tight control of a number of process parameters (listed in Table 1) to achieve consistent coatings. The deposition rates are also slow but this can be resolved by using multiple coating systems (a LP-CMS coating system is reasonably affordable).

A picture of the Dycomet™ LP-CMS coating system and a schematic of the coating process are shown in Figure 2 (a) and (b) respectively. To achieve the coatings deposition the metal particles are accelerated to very high velocities in a stream of carrier gas. The gas is heated before it enters a convergent–divergent de-Laval type nozzle. The feedstock powder is injected in the stream of carrier gas as it accelerates and cools down in the divergent section of the nozzle due to expansion. The accelerated solid particles then deform plastically upon impact with the substrate to form a dense coating.
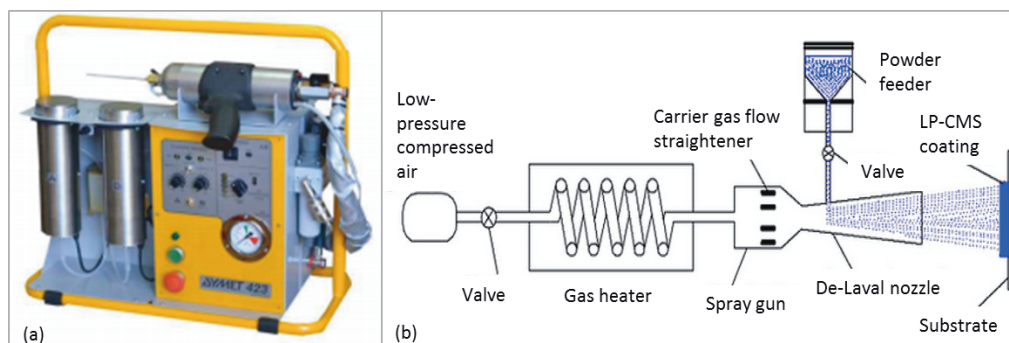

Figure 2: (a) Dycomet™ D-423 LP-CMS coating system, (b) a schematic of LP-CMS coating process adapted from (Papyrin, 2007)

Table 1: LP-CMS coating process parameters

Spray Process	Feedstock Material	Substrate	Environment
• Type of a carrier gas – air, helium, nitrogen • Carrier gas operating pressure and temperature • Nozzle geometry, i.e. convergent-divergent aspect ratio, cross-sectional profile etc. • Nozzle material • Nozzle stand-off distance from the substrate • Angle of strike between spray jet and the substrate • Deposition rates and scanning rate of the substrate/nozzle	• Composition of the feedstock material • Mechanical and metallurgical properties of the feedstock material • Particle size and normal distribution • Purity and oxygen content of the feedstock material	• Mechanical and metallurgical properties of the substrate material • Cleanliness and defect free surface of the substrate material • Surface roughness and profile • Temperature of the substrate • Thermal conductivity and coefficient of thermal expansion of the substrate material	• Cleanliness of the deposition environment • Relative humidity, dew point and temperature

A comparison of the spray temperature and the spray velocity for various types of metallic coating processes is shown in Figure 3. The possibility of a phase transformation and oxidation of a coating material increases with increasing of the process temperature. This is especially a concern where a material is heated beyond the melting temperature. The oxidation and phase transformation of a sprayed material will cause unwanted porosity, inclusions, and defects in the coating microstructure. Additionally, the inside out cooling of the deposited coating will cause build-up of undesirable tensile residual stresses, which will severely impair the coating fatigue strength and restrict the applicable thicknesses of the coating. Contrary to the effects of the coating process temperature, an increase in the spray velocity results in the reduction of the coating porosity with enhanced inter-lamellar cohesion of the microstructure. The LP-CMS coating process involves low temperature (typically <100 ˚C temperature in the divergent stage where the feedstock powder is injected in the nozzle) and supersonic particle velocities up to 600 m/sec. This unique low-temperature and high-impact deposition process gives LP-CMS coatings their characteristic low porosity microstructure with built-in compressive residual stresses. The low porosity is beneficial to enhance the coating resistance to corrosion and fatigue, whilst the built-in compressive residual stresses are desirable to improve the mechanical and fatigue strength of the coating.
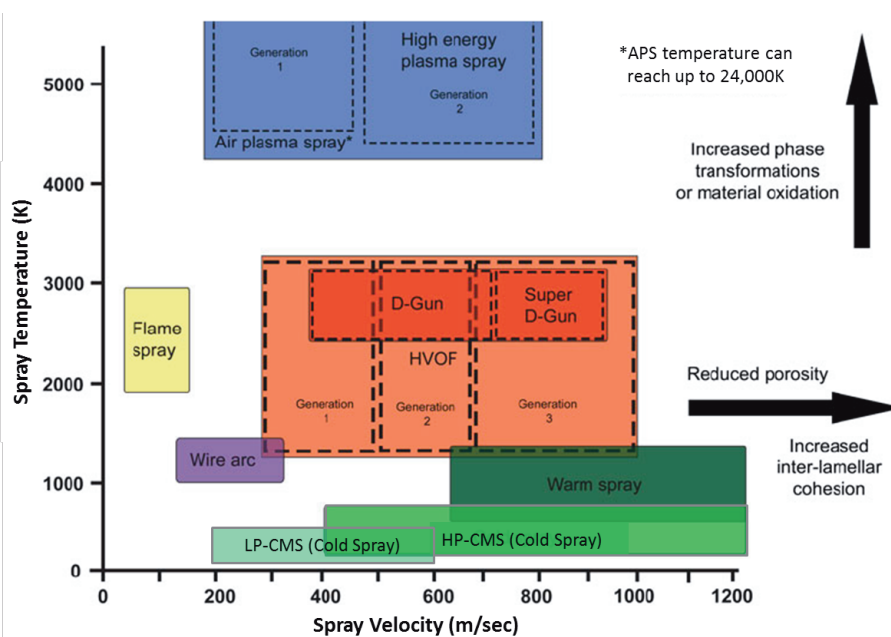

Figure 3: Spray temperature vs velocity comparison of various metal coatings processes, adapted from (Ming Ang et al, 2013)

4. Qualification testing of the LP-CMS coatings

The objective of the qualification testing was to investigate the suitability and robustness of the LP-CMS coatings for application in repair/restoration and preservation of the ship components. The assessment included qualification testing of metallographic, mechanical, and corrosion properties of the coatings. The test programme was designed to align with the following standards: MIL-STD-3021 (material deposition, cold spray, 4th Aug 2008) and Lloyds Register MQPS15-1 (materials and qualification procedures for ships, Book L, 1st Sept 2013).

4.1.   Production of the LP-CMS coating test samples

The LP-CMS process can be used for depositing a number of materials and alloys that are typically softer than the hardness of low carbon steel such as aluminium, copper, tin, antimony, silver, lead, zinc, nickel and their alloys. However, in context of marine applications, Al-alloy and CuZn-alloy will be the obvious choice for this study as there is precedent of these materials being used in the marine industry for corrosion protection.

The LP-CMS coatings were deposited on low-carbon steel (S355-J2) panel size 200 x 100 x 3mm. The panels were grit blasted to grade Sa 2½ (ISO 8501-1) with surface roughness aimed at >70 μm (R_t). The coatings were applied using an automated X-Y scanner. The required coating thickness was achieved with two consecutive passes of the spray gun, details of the deposited LP-CMS coating test samples and main process parameters are summarised in Table 2.

For corrosion test, one-half of the test panel was coated with Intershield-300 paint coating (320μm DFT) as shown in Figure 4 (a). This resulted in distinct 4-qudrants on the test panel, comprising: 'quadrant (i)' in the bottom right-hand corner – the grit blasted bare steel substrate, and then clockwise from there, 'quadrant (ii)' – paint coating + steel substrate, 'quadrant (iii)' – paint coating + LP-CMS coating + steel substrate, and 'quadrant (iv)' LP-CMS coating + steel substrate.

Table 2: LP-CMS coating test samples and main process parameters

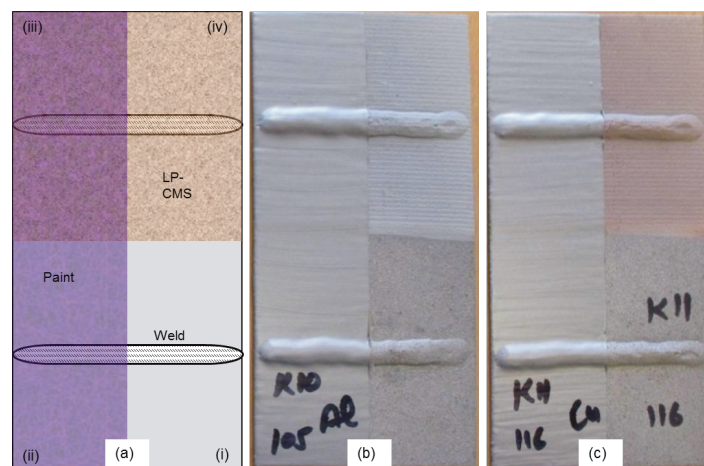| Coating Type	Material Composition (wt.%)	Nozzle Type	Temperature Setting	Input Air Pressure (bar)	Powder Feed Rate (g/sec)	Coating Thickness (mm)
Al-alloy	Al 60-70% Al$_2$O$_3$ 30-40%	Round	T3	6.2	0.55	0.3 ±0.05
CuZn-alloy	Cu 30% Zn 40% Al$_2$O$_3$ 30%	Round	T3	6.2	0.52	0.3 ±0.05

Figure 4: (a) A schematic of LP-CMS test samples, (b) Al-alloy, (c) CuZn-alloy coated test samples

4.2. Surface inspections of the LP-CMS coatings

The surface topography plays an important role in performance of functional coatings. The actual surface area is directly related to the surface finish (roughness), i.e. the surface area is the summation of the magnitude and number of peaks and troughs in a measured surface. The total surface area and the size/shape of the surface features play a critical role in the material degradation process. Increase in surface roughness will promote erosion, corrosion, and biofouling of material. However, in some instances the rougher surface finish is considered desirable, i.e. promoting adhesion and mechanical interlocking between the substrate and the coating. The surfaces of LP-CMS coating were inspected visually and with 2D/3D roughness measurement techniques.
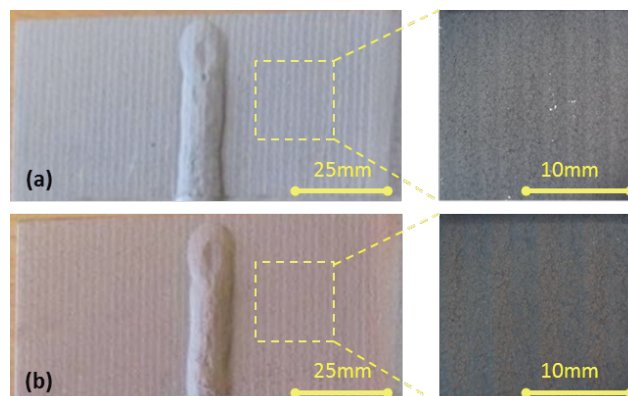

Figure 5: Visual and stereoscope inspection of (a) Al-alloy coating, (b) CuZn-alloy coating

4.2.1. Visual inspections

The coating test samples shown in Figure 4 (b) & (c) and Figure 5 (a) & (b) were examined visually with and without aided magnification. Both, Al-alloy and CuZn-alloy, coatings appeared free from any form of surface imperfections such as inclusions, blisters, lifting, cracking or spalling. The direction of the coating spray and ridges from the spray step-over were evident on the surface of both coatings.

4.2.2. Surface roughness measurement

The surface roughness was measured with a benchtop Taylor-Hobson contact surface profilometer with 2 μm diamond-tip stylus. The test parameters were selected as per ISO-4288 standard for surface roughness measurement.

In this study, for the sake of simplicity only the 'R_t' surface roughness parameter was considered, it represents the sum of the deepest valley and the highest peak in the measured surface. The measured values of 'R_t' were 132 μm, 170 μm and 142 μm for the grit blasted substrate, Al-alloy coating, and CuZn-alloy coating surface respectively. The surface of LP-CMS coatings was rougher than the bare steel substrate. The increase in the surface roughness of the coatings is likely to have been caused by the micro-impacts resulting from the sprayed particles and the surface undulation caused by the step-over raster of the spray gun. The scale and spread of the roughness features in the surface of the LP-CMS coatings is apparent from the 3D surface maps shown in Figure 6 (measured with an infinite focus Alicona microscope).
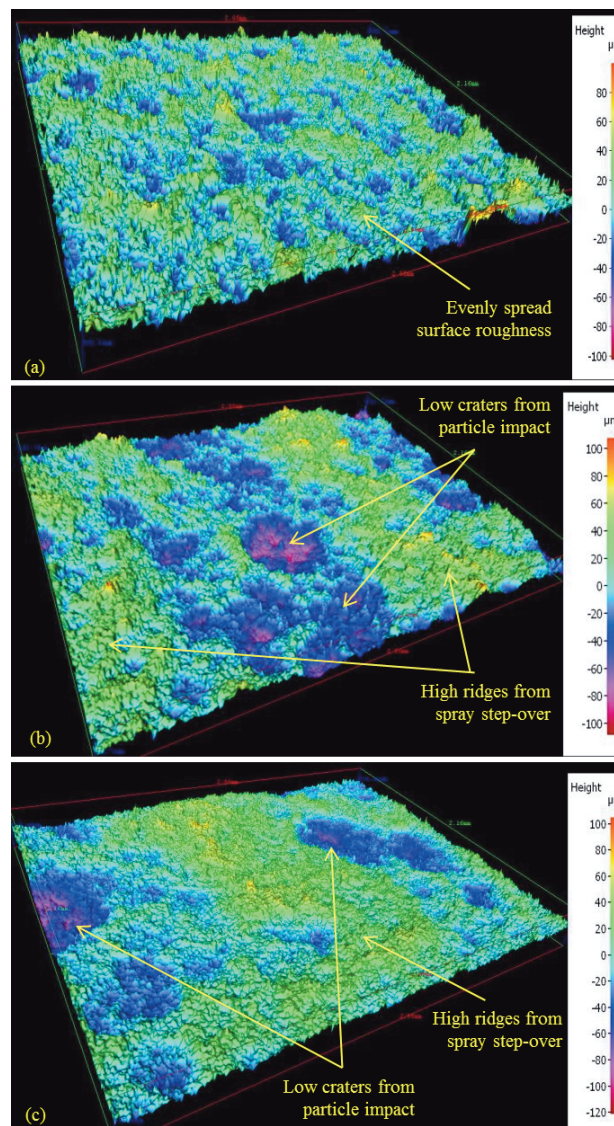

Figure 6: 3D surface scans (3.0 x 2.2 mm): (a) grit blasted steel substrate, (b) Al-alloy coating, (c) CuZn-alloy coating

4.3.   *Metallographic inspection of the LP-CMS coatings*

The microstructure of a material has a significant influence on the overall mechanical and material properties. The shape, size, and orientation of the microstructural grains, different alloying phases and their distribution, oxides, porosity and inclusions, all have a direct influence on the material properties of sprayed metallic coatings. The microstructure of a material, the material properties, and the material degradation process are interdependent, i.e. the material degradation process is directly related to the material properties such as modulus of elasticity and hardness, which in turn depends on the material microstructure.

The microstructure and metallographic features of Al-alloy and CuZn-alloy coatings were investigated using optical microscopy, scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDX). Micro-sections of the coatings were prepared as per ASTM E1920-03 standard. The average cross-sectional thickness of the coatings was measured as 0.32±0.4 mm for Al-alloy coating, and 0.34±0.3 mm for CuZn-alloy coating. The thickness of the coatings was mostly within tolerance.

The backscattered scanning electron (BSEM) images and EDX elemental maps of the Al-alloy coating are shown in Figure 7 (a). The dark-grey Al_2O_3 (alumina) particles are distributed evenly within the overall light-grey Al matrix of the coating. The very dark black spots represent the porosity, which is mainly concentrated around the alumina particles and at the substrate-coating interface. It is observed that the coating porosity may have been caused by the shadowing effect from the alumina particles. The darker black/brown areas in 'O' and 'Al' Ka1 elemental maps shows the spread of alumina particles. The light yellowish/orange colour areas in 'Al' Ka1 map represent the Al matrix. The two major constituents of the Al-alloy coating, Al and alumina, are distributed well within the coating matrix.
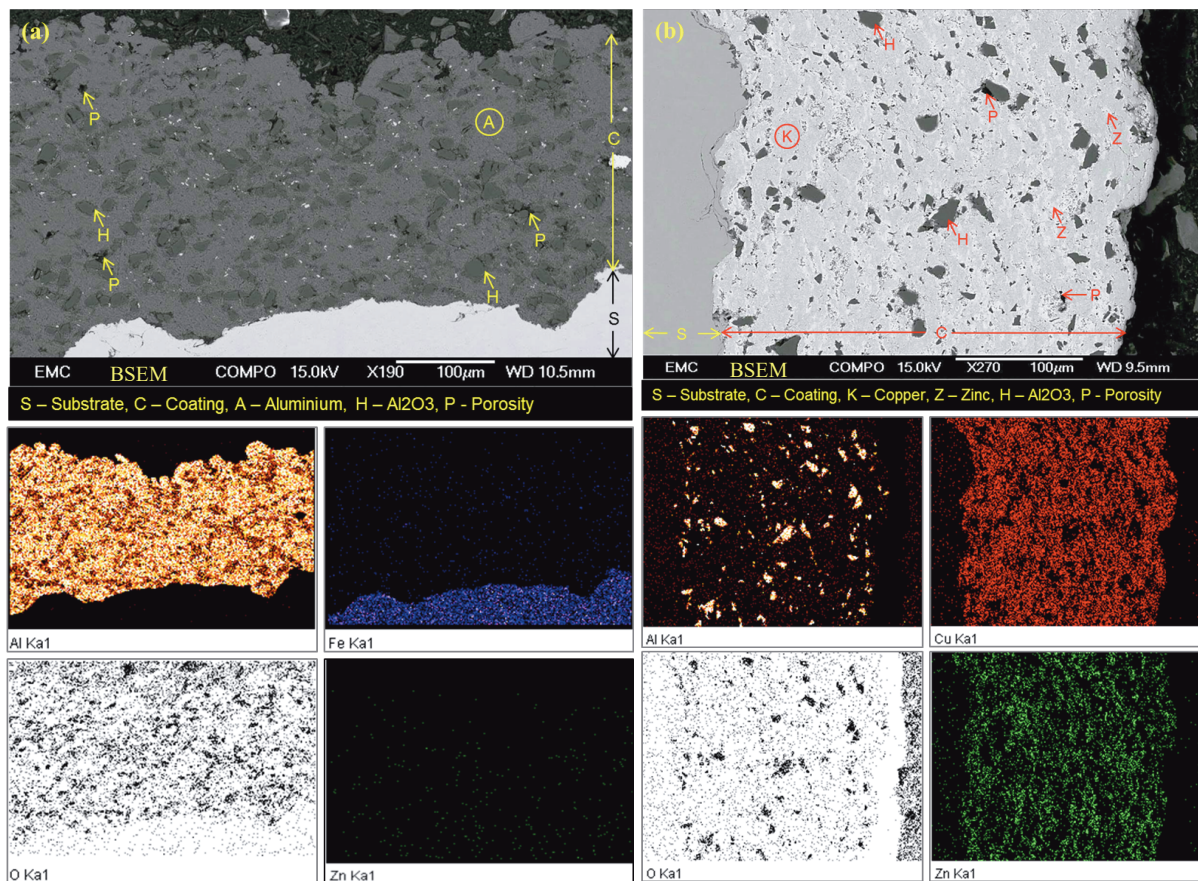

Figure 7: BSEM and EDX images of microstructural analysis, (a) Al-alloy coating, (b) CuZn-alloy coating

The BSEM image and EDX elemental maps of the CuZn-alloy coating are shown in Figure 7 (b). In the BSEM image, copper is shown as light grey colour, zinc as bright whitish colour, alumina particles as dark grey irregular shape spots, and very dark spots (mainly around alumina particles) is the porosity. The EDX elemental maps also show a good distribution of the coating main constituents – Cu, Zn, and alumina. The dark black spots in 'O' Ka1 elemental map and bright orange spots in 'Al' Ka1 map represents the alumina particles. The green colour in 'Zn' Ka1 and red colour in 'Cu' Ka1 maps represents the distribution of Zn and Cu respectively.

It is evident from the metallographic analysis of the LP-CMS coatings that the overall coating microstructure is mainly heterogeneous but the constituent elements are well distributed in the coating microstructure.

4.4.   *Porosity inspection of the LP-CMS coatings*

The presence of porosity in a coating will affect its mechanical and corrosion performance. Increased coating porosity will weaken the coating microstructure, and pose increased risk of crack initiation and spreading along the porosity in the coating, thus causing a reduction in the coating fatigue strength. Any unsealed porosity in the coating will also create a path for environment permeation, thus causing corrosion and delamination of the coating from the substrate interface.

The porosity of LP-CMS coatings was measured with an image analysis technique similar to the one described in ASTM E2109-01 "test methods for determining area percentage porosity in TMS coatings". Several images of the coating microstructure were analysed with 'ImageJ' software. The results of the average area porosity of the coatings are presented in Figure 8. The porosity in Al-alloy coating was measured ~2.4%. In comparison, the flame and arc sprayed Al-alloy coatings have been reported to possess ~14% and ~24% porosity respectively (Kawaguchi et al, 2017). The porosity in CuZn-alloy coating was measured as low as 0.8%. It is desirable to have the coating porosity as low as possible to achieve better mechanical and corrosion performance in the marine environment.
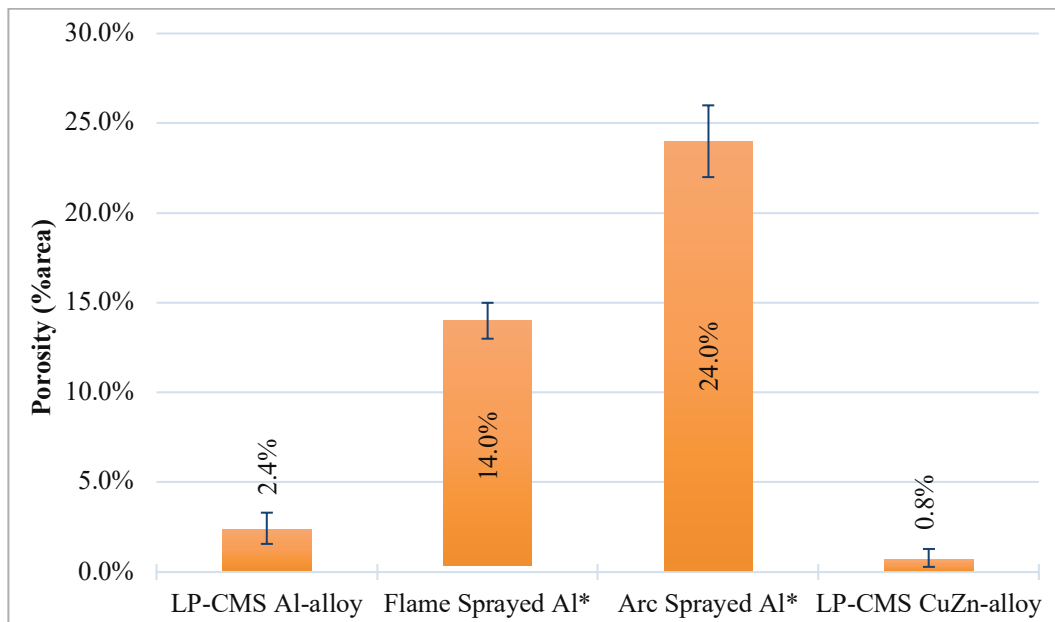

Figure 8: Porosity comparison of LP-CMS and flame/arc sprayed TMS coatings (*Kawaguchi et al, 2017)

4.5.   *Mechanical properties of the LP-CMS coatings*

4.5.1. Nanoindentation test

The hardness and young's modulus of elasticity of the LP-CMS coatings were obtained from nanoindentation load and displacement tests conducted as per ISO 14577 standards. The average values of the hardness and young's modulus of elasticity of the two coatings are summarised in Table 3.

It is apparent that the hardness and young's modulus of the LP-CMS coatings are far superior in comparison to the bulk materials of the same composition. These results agree with the findings reported in the literature (Kim et al, 2011), which state that the mechanical properties such as ultimate tensile strength, yield strength, and young's modulus of elasticity of the cold metal sprayed (CMS) coatings is better than the wrought material of similar composition. The superior material properties are achieved because particles in the CMS process are less susceptible to thermal oxidation, and high velocity impact creates a dense and well-consolidated coating microstructure. The hardness and modulus of elasticity of CuZn-alloy coating is better than the Al-alloy coating, which will make CuZn-alloy coatings better suited for the applications where better mechanical properties are required.

Table 3: Nanoindentation hardness and young's modulus of elasticity of LP-CMS coatings

Coating/ Material Type	Hardness, H (GPa)	Young's Modulus of Elasticity, E (GPa)
Al-alloy LP-CMS coating	0.98 ± 0.20	92 ± 11
Al alloy UNS A95005 (Matweb Database)	0.44	69
CuZn-alloy LP-CMS coating	1.83 ± 0.41	122 ± 15
Cold Spray Cu coating (Yang et al, 2018)	1.71	135.45
CuZn alloy UNS C28000 (Matweb Database)	0.95	105

4.5.2. Adhesion and ductility test

The adhesion between the coating and substrate, and the coating ductility is very important to ensure good performance in-service. Poor adhesion will cause the delamination of the coating in-service, thus leaving the substrate underneath unprotected and susceptible to environmental corrosion. The ductility of a coating indicates whether the coating will adequately endure mechanical and thermal stresses and strains in-service without failure.
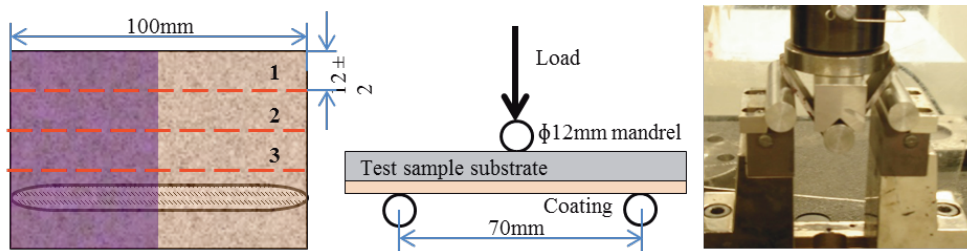

Figure 9: 3-point bend test used in qualitative assessment of adhesion and ductility of LP-CMS coatings
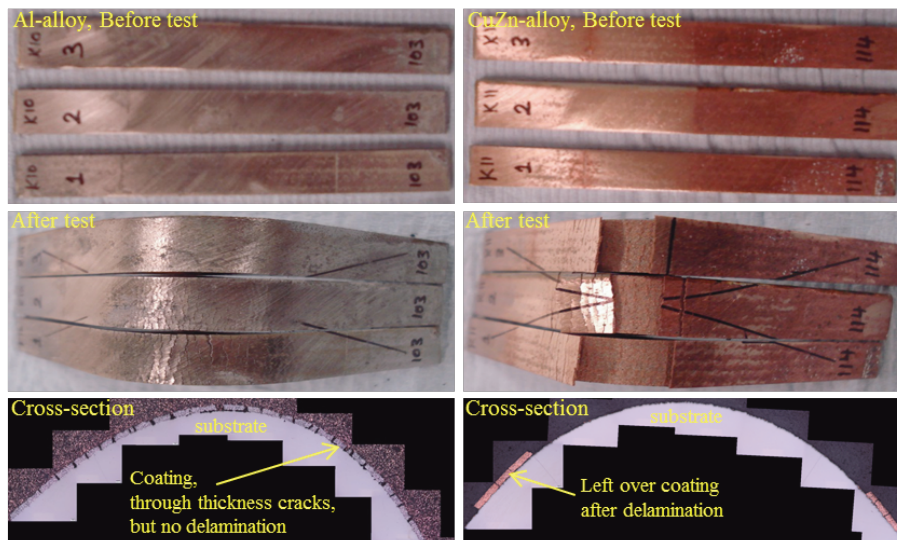

Figure 10: Al-alloy and CuZn-alloy test samples after 3-point bend test

A 3-point bend test was performed as per ASTM E290 standard to assess adhesion and ductility of the LP-CMS coatings. A schematic of the 3-point bend test and the test samples is shown in Figure 9. For both coatings, 3-off test samples were bent transverse to the direction of the coating deposition. The test samples were bent over a ϕ12 mm stainless steel mandrel with coating facing away from the mandrel in one rapid downward stroke (10 mm/sec) to produce ~110° bend. The coating is considered to have good adhesion and ductility if it does not completely delaminate from the substrate. The through thickness cracks in the coating along the bend edges are considered acceptable as long as there is no coating delamination from the substrate.

As shown in Figure 10, the Al-alloy coating showed the best adhesion and ductility. There were some through thickness cracks in the coating along the bent radius, but no coating delamination from the substrate. The through thickness cracks did not stretch along the whole width of the test sample, they were rather concentrated at the side edges where the stresses and strains were the highest due to bending. However, CuZn-alloy coating did show complete delamination from the substrate along the bent radius. A pull-off adhesion test

similar to ASTM D4541 standard has been planned to measure the exact adhesion and cohesion strength of the LP-CMS Al-alloy and CuZn-alloy coatings. Most maritime applications require adhesion and cohesion strength of >1,000 psi (6.9 MPa) from in-service functional coatings.

4.6. Corrosion testing of the LP-CMS coatings

Corrosion is the most common material degradation mechanism in the marine environment. Corrosion adversely affects the reliability, availability, and upkeep cost of naval ships. A recent study on the 'cost of corrosion to US Navy' estimated that the total annual cost of corrosion was ~$8.6 billion, plus ~392,040 non-available days of Navy equipment and ground assets (Herzberg, 2018).

In this study, the corrosion performance of LP-CMS coatings was evaluated in atmospheric (salt-spray) and natural immersion environment.

4.6.1. Accelerated salt-spray corrosion test

Two test samples of Al-alloy and CuZn-alloy coatings were exposed to an accelerated salt-spray corrosion test similar to ASTM B117 standard. The corrosion performance of most functional coatings including the paint coatings is tested and accepted following an accelerated salt spray corrosion test.

A carbide tip scriber was used for creating artificial damage in the paint and LP-CMS coatings. It was observed that the hand scribing was unable to cut through the LP-CMS coatings 'quadrant (iv)' (Figure 4 (a)) to expose the steel substrate underneath the metallic coatings, but for the paint coatings, the scriber did expose the steel and LP-CMS surfaces underneath the paint coating in 'quadrant (ii)' and 'quadrant (iii) respectively. Quadrant (i) was also painted because the salt-spray environment was considered too aggressive for the bare steel substrate to survive the test duration.

Figure 11: Accelerated salt-spray (ASTM B117) corrosion testing of Al-alloy and CuZn-alloy LP-CMS coatings

For Al-alloy coating 'quadrant (iv)' showed copious amount of clear gel like Al hydroxide on its surface after 800 hrs of salt spray test, but there were no rust marks on the coating surface as is shown in Figure 11. This implied that the Al-alloy coating was protecting the substrate underneath from the corrosion. On quadrant

(iii) Al-alloy coating with scored paint coating, there were blisters around the scribe damage in the paint coating. The forming of blisters in the paint coating caused accelerated depletion of the Al-alloy coating underneath. This is a well-understood form of corrosion in marine environment (Sumon et al, 2013). The blisters started to grow parallel to the substrate after just 96 hours of salt spray. However, when the blisters in the paint coating were taken-off, no corrosion to the steel substrate underneath was observed, but the Al-alloy coating under the blisters was fully consumed. In quadrant (ii) as expected, the steel substrate corroded extensively along the scribed damage created in the paint coating.

For CuZn-alloy coating, 'quadrant (iv)' also showed large build-up of Zn hydroxide on the coating surface. The zinc from CuZn-alloy coating sacrificial protected the steel substrate and the more noble element 'copper' within the coating matrix. Test sample #2 showed some rust spots close to the root of the weld seam and on the border with the painted 'quadrant (i)'. The other rust streaks on the test panel were superficial, likely to have been caused by the poor sealing of the side edges and back surface of the steel substrate. Further investigation of the rust spots on the test sample #2 confirmed there was a defect in the CuZn-alloy coating close to the root of the weld seem. The shadowing of coating spray by the weld seam possibly caused the defect in the coating. The paint coating applied to 'quadrant (i)' did not fully seal the border with the CuZn-alloy coating, thus causing spots of local corrosion on the unprotected steel substrate. The results of accelerated salt-spray testing (atmospherics corrosion) showed that both, Al-alloy and CuZn-alloy, coatings will sacrificially protected the steel substrate.

4.6.2. Natural immersion test

A tidal dock at the Portsmouth Naval Base was used for the natural immersion corrosion test. Two test samples of Al-alloy and CuZn-alloy coatings were mounted on an immersion trolley and submerged in the tidal dock resting on a north-facing wall. The bottom end of the trolley was ~0.5m clear of the seawater level during the lowest tide. The samples marked as #1 spent $1/3^{rd}$ of their total test time out of the seawater due to the tidal variations. The total duration of the immersion test was ~2,250 hours. The 'quadrant (i)' of the test sample was left as bare steel (uncoated) for the immersion test. The bare steel will act as a cathode for the LP-CMS coating when submerged in seawater. This will present the worst case scenario for immersed corrosion.

As shown in Figure 12, there was large build-up of Al hydroxide and biofouling on the Al-alloy coating after ~3 months of immersion in the seawater. The Al-alloy coating was almost fully consumed as it sacrificially protected the steel substrate in the uncoated quadrant (i) and underneath the Al-alloy coating. The test sample #1 had less severe depletion of Al-alloy coating as it spent ~$1/3^{rd}$ of its time out of the seawater. The complete depletion of the Al-alloy coating suggests that it will not be suitable for the application in fully immersed seawater environment, especially in the worst-case scenario where a large cathodic area (bare steel) is present.

The CuZn-alloy coating showed no signs of depletion and no build-up of biofouling at all after 3 months of immersion. The coating appeared in as good condition as it was before the test. The zinc from the CuZn-alloy coating sacrificially protected the steel substrate, and copper prevented the build-up of biofouling. The bare steel 'quadrant (i)' on sample #1 rusted because of the sodium chloride drying on its surface. This test sample spent $1/3^{rd}$ of its total test time out of the seawater.

The CuZn-alloy coating behaves similar to brass in seawater, there is minimal to no leaching of Cu ions from the coating, and Zn sacrificially protects the steel substrate and the nobler copper element of the coating. The results of an inductively coupled plasma mass spectrometry (ICP-MS) test summarised in Table 4. The result shows the amount of metallic ions dissolved into 200 ml of electrolyte (3.5% NaCl) from the test area of ϕ12 mm of LP-CMS coatings in a month long electrochemical corrosion test. The amount of Cu dissolved from the CuZn-alloy coating was ~660 ppb (parts per billion). To put this into perspective, the EU and WHO guidelines for Cu dissolved in drinking water is 2 mg/l (2,000 ppb). The overboard discharge of cooling seawater from naval ships typically contains up to 1.45 mg/l (1,450 ppb) of Cu (US Environmental Protection Agency report EPA-842-R-99-001 – Appendix A: seawater cooling overboard discharge).

Table 4: ICP-MS analysis of elements dissolved into artificial seawater during a month long corrosion test

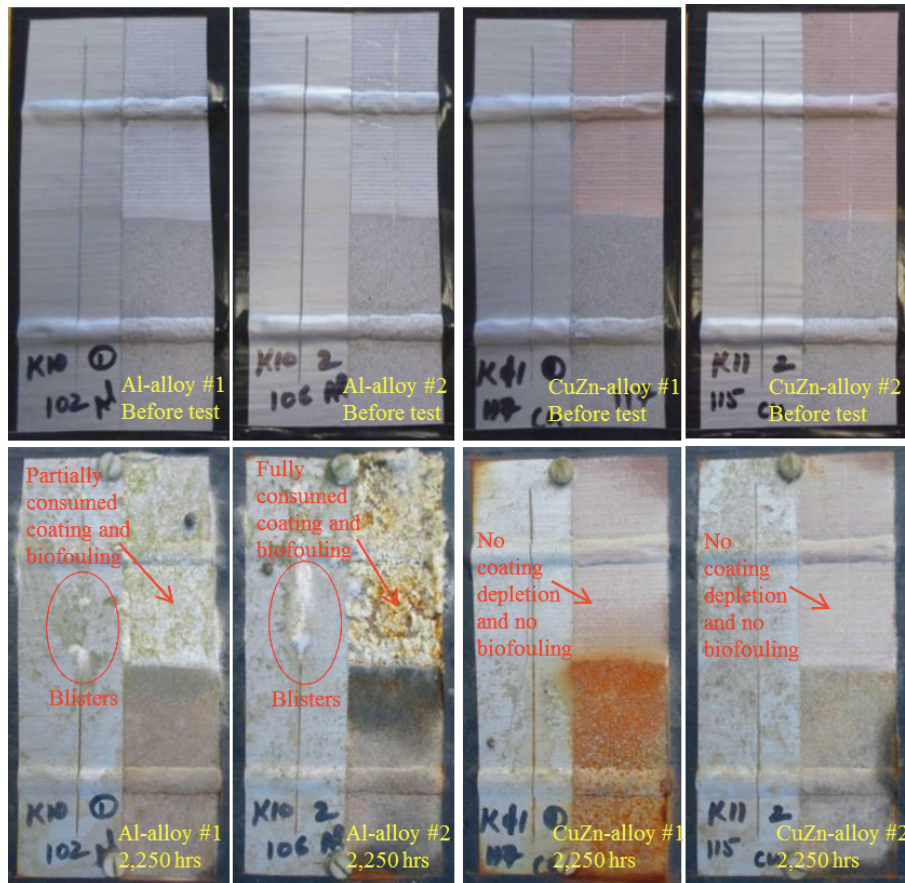| Test Sample	Sodium (Na), ppb	Aluminium (Al), ppb	Iron (Fe), ppb	Copper (Cu), ppb	Zinc (Zn), ppb
Reference Electrolyte	17,860,000	77	29	3	41
Electrolyte - CuZn-alloy	44,980,000	134	99	660	16,048
Electrolyte - Al-alloy	36,300,000	6,040	72	39	43

Figure 12: Natural immersion corrosion testing of Al-alloy and CuZn-alloy LP-CMS coatings

5. Case studies

The advantage of LP-CMS coating process is that it can be used for either surface engineering the new components to preserve/protect them from in-service material degradation, and/or to repair and restore any non-structural damage in operational components. This flexibility of the LP-CMS coating process is demonstrated with help of two case studies:

- A seawater valve disc with extensive damage on its surface was repaired and restored to its original shape and size,
- A damaged pump impeller was repaired and then a metallic coating with antifouling properties was applied over the repaired surface to prevent in service microbial induced corrosion (MIC) of the impeller surface.

5.1.   *Repair and restoration of a seawater valve disc using LP-CMS coatings*

A seawater valve disc before and after the LP-CMS coating repair is shown in Figure 13. The bronze valve disc had extensive erosion-corrosion damage, which in places was up to 2 mm deep. The damaged surface/profile of the valve disc meant that it was not sealing properly with the valve seat, thus passing seawater when it should not be in the fully shut position.

The damaged areas in the valve disc were locally grit blasted or prepared mechanically to receive CuZn-alloy coating. The main steps of LP-CMS repair process are also shown in Figure 13. The repaired valve disc passed two qualification tests: non-destructive dye penetrate test was performed to check whether there were any defects in the repaired areas, and 1.5 x operating pressure test was performed to check the repaired valve disc will operate safely in a functional system valve. There is now a plan to install the repaired valve disc on a harbour ship as part of a minor trial.

The ability to repair and restore damaged components can realise significant cost savings and can improve the turnaround time for a typical maintenance period by eliminating the need to rely on a specialised supply chain that often has long lead times and high material cost. The cost savings for repairing a valve instead of

buying a new one can be an order of magnitude less. The reclamation of damaged parts instead of replacement will also save unnecessary wastage of material thus helping the environment.

Figure 13: Repair and restoration of a seawater valve disc with LP-CMS coatings

5.2.   *Repair and surface engineering of a pump impeller using LP-CMS coatings*

High-pressure seawater (HPSW) pump impeller before and after LP-CMS repair and application of an antifouling coating is shown in Figure 14. The bronze impeller had extensive material degradation in form of both shallow and deep corrosion pits. The damage appeared to be similar to microbial induced corrosion (MIC). The stagnated seawater conditions created by infrequent operation of some HPSW pumps can leave them vulnerable to MIC attack.

The damage in the impeller disc was repaired with CuZn-alloy coating and then a ~100 μm Cu-alloy coating was applied as an anti-microbial preservation surface. The reasoning for using Cu coating was that it will function as an anti-microbial surface thus preventing the attack of MIC. The sprayed Cu coating is fully dense, therefore, it is expected that it will not cause any worse release of Cu ions then the commonly used Cu and CuNi90/10 tubing in on-board seawater systems.

Figure 14: Repair and preservation of a HPSW pump impeller

Unfortunately, the impeller repaired in this case study had some large fatigue cracks in the disc and the impeller hub. Although, the cracks were repaired, the impeller is considered unsafe for any in-service minor trials until further testing is done to validate the integrity of the repair scheme. However, this case study does show that it is possible to deposit functional coatings such as antifouling Cu coating on a component to reduce the risk of in-service material degradation such as MIC. Other customised surface engineering coatings can be applied with the LP-CMS coating process to target the specific material degradation mechanisms and operation environments.

The use of LP-CMS to deposit functional coatings can bring a huge amount of cost savings. The initial cost of application for LP-CMS coatings is higher due to slow deposition rates, but the life expectancy/durability of these coatings also tends to be higher. A desktop study on using LP-CMS Al-alloy coating for the weather deck application showed that for a "cost/year/square meter" scenario, the LP-CMS coating will offer a cost reduction of 33% and 500% respectively when compared to conventional epoxy paint coatings and TMS coatings.

6. Conclusions

The results of qualification testing presented in this paper show that LP-CMS coatings are dense, uniform, and free from unwanted inclusions and defects, and have mechanical properties that match or exceed the properties of similar composition bulk materials.

The accelerated salt spray corrosion test is widely used for the validation and qualification of most functional coatings, including paint coatings. The results of accelerated corrosion testing showed that composition (functional material elements) and operational environment would significantly influence the corrosion performance of LP-CMS coatings.

The results of the accelerated corrosion testing of LP-CMS coatings showed that Al-alloy coating will be better suited to operational environments where protection from the atmospheric corrosion and/or cyclic loads (fatigue/fretting) is required. However, this coating will not be suitable for full-immersed seawater environment if the coating surface is unsealed and there is presence of a large cathodic surface (i.e. uncoated steel).

The CuZn-alloy coating due to its low porosity, high hardness, good antifouling, and corrosion resistance will be suited to operational environments where protection from erosion, corrosion and biofouling is required. This coating will be suited to both atmospheric and fully immersed marine environment.

The case studies presented in this paper showed that LP-CMS coating process would be suitable for both repair (reclamation) and preservation (surface engineering) of ship components. The use of LP-CMS coatings in shipbuilding and fleet services will likely present significant cost savings with improved turnaround times. However, further trials and testing on in-service platforms is needed to build up the experience and confidence in use of LP-CMS coatings in marine environment. Cooperation from the fleet owners and maintainers will be needed to plan and perform minor trials on operational ships. The repaired valve disc is now planned to be used in a minor trial on a harbour ship.

There are a number of other test samples that are now being tested to validate the use of Al-alloy LP-CMS coating in weather deck applications. There is also an on-going activity to achieve the type approval of LP-CMS coating process from a leading Classification Society.

7. Acknowledgements

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