Feasibility Study of Dealloying Corrosion Prevention in Manganese Aluminium Bronze (MAB)

Thunyaphorn Piankijsakul[1], Napachat Tareelap[1],

Kaysinee Sriraksasin[2] and Nakorn Srisukhumbowornchai[1]

[1]Division of Materials Technology, School of Energy, Environment and Materials,

[2]Research, Innovation and Partnerships Office

King Mongkut's University of Technology Thonburi, Bangkok, Thailand

Email: thunthun.tp@gmail.com

ABSTRACT Due to Manganese Aluminium bronze (MAB) used in marine applications deteriorated in the form of de-alloying corrosion making the structure failed, this research is aimed to study the feasible method to prevent it from corrosion. The selected methods were metallic thermally-sprayed aluminium bronze (Al-Cu) and aluminium (Al) coatings, polymer coating and cathodic protection by installing aluminium sacrificial anode. The prevention ability was conducted by immersion testing in natural brackish water (usage condition) for 180 days. After testing, the samples were visually inspected and cross-sectional metallographic studied. Corrosion analysis was also performed using electrochemical techniques; anodic polarization and long-term open circuit (OCP) measurements. The results stated that thermally-sprayed aluminium coating and cathodic protection using aluminium sacrificial anode could protect MAB from deterioration more effective than polymer and aluminium bronze (Al-Cu) coatings. It is indicated by none of de-alloying corrosion was observed. In contrast to polymer coating and thermally-sprayed aluminium bronze coating (Al-Cu), de-alloying corrosion was observed underneath the coatings because of delamination and degradation of polymer coating and blistering of aluminium bronze coating accordingly.

KEYWORDS Manganese Aluminium bronze (MAB), De-alloying corrosion, Cathodic protection, Thermal spray coating, Polymer coating

INTRODUCTION

Manganese Aluminium Bronze (MAB) is a copper-based alloy which is widely used in marine applications. Its principle alloying elements are manganese, aluminium and nickel. The metal is locally deteriorated in the form of de-alloying corrosion driven by micro-galvanic coupling between two phases (Meigh, 2000). This phenomenon leads to leave porous copper; therefore, its mechanical properties decreases and fails finally. To overcome this problem, this research aims at studying feasibility of de-alloying corrosion prevention to extend life of this metal by means of metallic coating (Thermally-sprayed aluminium bronze and aluminium coatings), polymer coating and cathodic protection using aluminium sacrificial anode.

EXPERIMENT

Cast manganese aluminium bronzes (MAB) were cut into size of 5 cm x 5 cm. For thermally-sprayed aluminium bronze (Al-Cu) and aluminium (Al) coatings, MAB substrates were prepared by alumina blasting (white alumina #24); then, electric-arc sprayed with 1.6 mm diameter aluminium bronze and aluminium wires. They were then ground using grit paper up to No.800 for smoothening. The obtained coating was in the range of 300-500 µm thick. Bonding strength was controlled to ensure good bonding between coating and substrate. For polymer coating, MAB substrates were prepared according to the factory guidelines by grinding with No.80 grit paper then rinsing with DI water and acetone respectively. Base primer, a mixture of resin and hardener, was applied on the substrate by brushing. After air-dried, silicone top coat was applied and air-dried. Its thickness, measured by Surfix FN coating thickness gauge, was in the range of 70-80 µm. Adhesion of polymer coating was also examined followed ASTM D3359. In case of cathodic protection using aluminium sacrificial anode, MAB samples were prepared by grinding up to No.800 grit paper, rinsing with DI water, air-dried followed by attachment with anode. The specimens were corrosion studied by immersion test in natural brackish water (usage condition) for 180 days. After testing, the specimens were visually inspected. To examine de-alloying corrosion by optical microscope, it was prepared by cross-section, grinding, polishing and etching with a mixture solution of $FeCl_3$ and HCl for 5 seconds. Corrosion behavior was also studied by long-term open circuit measurements and anodically polarized the samples from open circuit potential (OCP) to 1 V versus Ag/AgCl reference electrode at a scan rate of 1 mV/s using Autolab PGSTAT30 potentiostat. The polarized samples were then cross-section and metallographic examination. It is noted that corrosion behaviour of un-prevented MAB was also studied for comparison reason.

ANALYSIS

1. Corrosion studied of un-prevented manganese aluminium bronze

Optical micrograph of MAB is shown in Fig. 1(a). Bright area was α phase (copper-riched phase) while dark area was β phase (aluminium-riched phase). The flower-liked precipitate was κ phase. After immersion test in natural brackish water for 180 days, the alloy underwent de-alloying corrosion (arrowed Fig. 1(b)). The corrosion onset appeared at β phase then propagated to α phase. The corrosion attack was driven by electrochemical potential differences or micro-galvanic coupling between α and β phases as explained elsewhere (Tareelap et al., 2013)

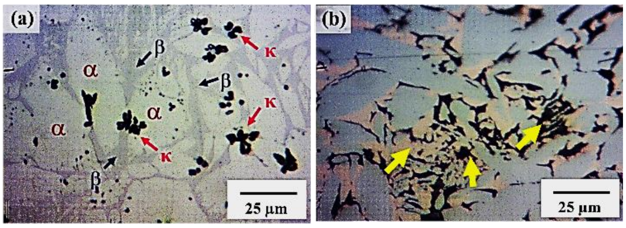

Fig. 1 (a) Optical micrographs of manganese aluminium bronze and (b) de-alloying corrosion found after immersion in natural brackish water for 180 days.

2. Corrosion studied of prevented-manganese aluminium bronze

2.1 Corrosion prevention approached by thermal-sprayed metallic coating

Appearance of thermal-sprayed aluminium bronze (Al-Cu) and aluminium (Al) coatings is shown in Fig. 2(a). After immersion test in natural brackish water for 180 days, blistering of Al-Cu coating was observed (circle) while the Al-coating was uniformly attacked which is indicated by white rust of aluminium entire the surface (Fig. 2(b)).

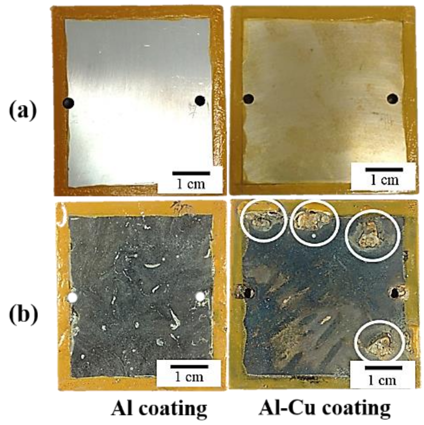

Fig. 2 Appearances of thermal-sprayed Al-Cu and Al coatings (a) before and (b) after immersion test in natural brackish water for 180 days.

Cross-sectional images of Al-Cu coating compared with Al coating exhibit in Fig. 3. The de-alloying corrosion (arrowed in Fig. 3(c)) was observed not only in Al-Cu coating but in MAB substrate as well. It is possible that once the blistering occurred, the delamination of coating happened. This occurrence was driven by galvanic coupling between coating and substrate (Zhao et al., 2005) or the penetration of electrolyte through micro-voids or pores in the coating (Marcela et al., 2012). Once the delamination occurs, the aggressive ions in corrosive environment attack the substrate; hence, corrosion is promoted. In contrast to Al coating, the delamination and corrosion underneath the coating were not observed. It is because of sacrificial property of aluminium coating (McCafferty, 2010) supplying electron (from dissolution) to prevent MAB substrate from corrosion.

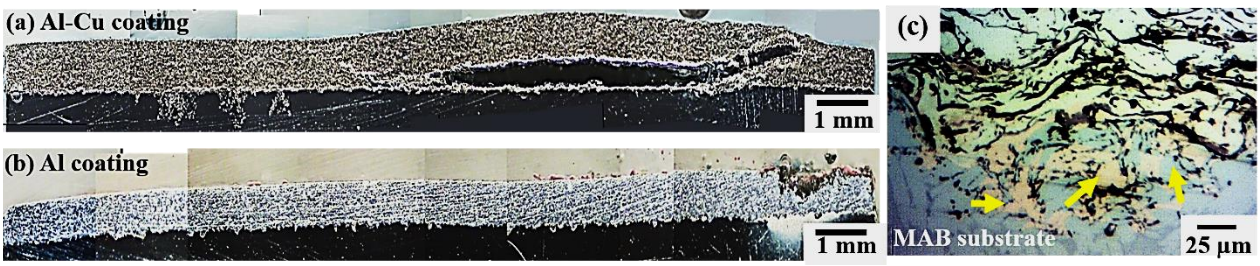

Fig. 3 Cross-sectional images of (a) Al-Cu and (b) Al coatings after immersion test in natural brackish water for 180 days, (c) dealloying corrosion underneath Al-Cu coating.

2.2 Corrosion prevention approached by polymer coating

Appearance of polymer-coated MAB before and after immersion in brackish water for 180 days is shown in Fig. 4. It is observed that the specimen turned to green after immersion test. The FTIR spectra (not shown) revealed some changes of polymer coating composition after the test. It is possible that polymer coating degraded during immersion test in brackish water. Moreover, the delamination (arrowed in Fig. 4(b)) of coating was observed after immersion test.

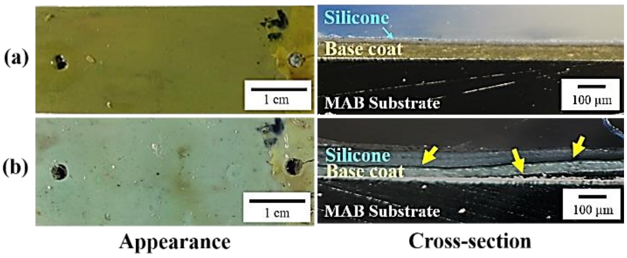

Fig. 4 Appearance and cross-sectional image of polymer-coated MAB (a) before and (b) after immersion test in natural brackish water for 180 days.

Cross-sectional images of polymer-coated MAB in Fig. 5 supported that de-alloying corrosion was found underneath the degraded and delaminated polymer coating only (arrowed in Fig. 5(b)) similar to that happened in Al-Cu coating as explained previously.

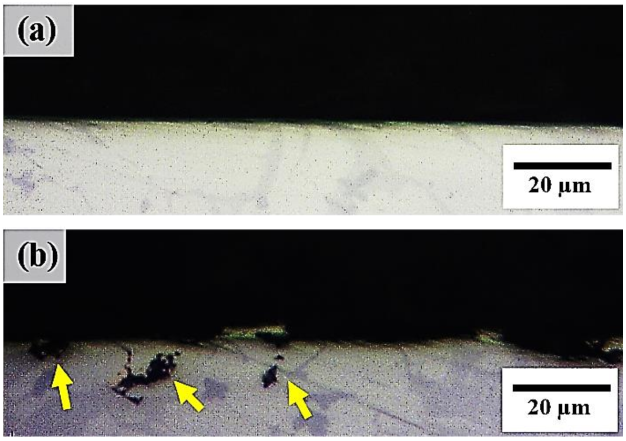

Fig. 5 Cross-sectional images of polymer-coated MAB (a) before and (b) after immersion test in natural brackish water for 180 days.

2.3 Corrosion prevention approached by cathodic protection using aluminium sacrificial anode

Fig. 6 shows the appearance of MAB prevented by installing aluminium sacrificial anode before and after immersion test. It is seen that none of de-alloying corrosion was observed even cross-sectional examination.

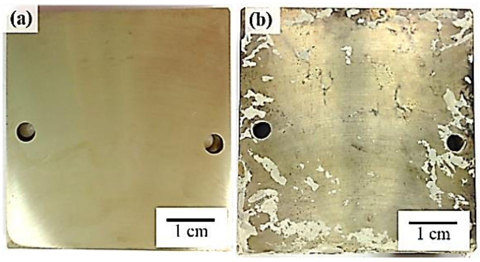

Fig. 6 Appearances of MAB prevented by installing aluminium sacrificial anode (a) before and (b) after immersion test in natural brackish water for 180 days.

To proof the effectiveness of corrosion prevention by sacrificial anode, long term open circuit potential (OCP) measurement was performed as exhibited in Fig. 7. It is evident that the MAB attached with anode had potential in the range of –0.82 to –0.84 V that less than MAB without anode about 650 mV. According to E-pH diagram of copper in Fig. 8, MAB attached with anode had potential in the immunity region meaning that this metal free from corrosion.

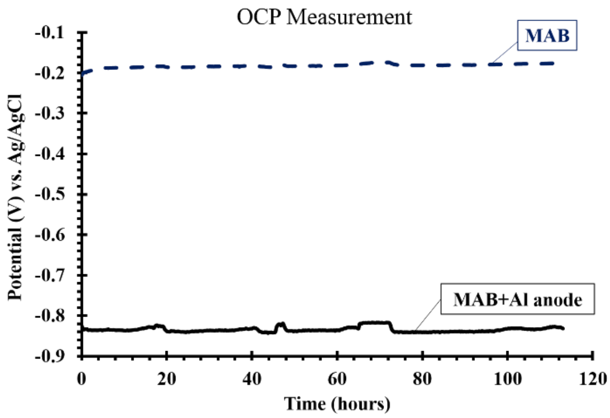

Fig. 7 Long term open circuit potential measurements of MAB attached with- and without sacrificial anode in 3.5% NaCl for 5 days.

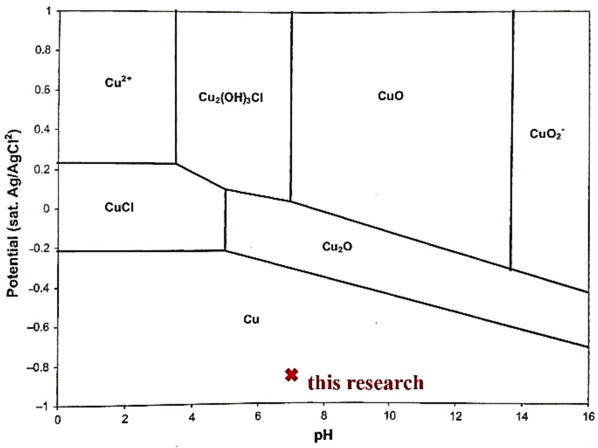

Fig. 8 E-pH diagram of copper for seawater (Copper-Chloride-water system) (Roger, 2010).

Corrosion behavior of MAB attached with- and without sacrificial anode was also studied by applied potential from OCP to 1V. The cross-sectional image of specimens after perform the test is shown in Fig. 9. It is evident that the specimen without sacrificial anode was attacked severely. The attacks were in the range of 10 μm depth and were observed at both of α and β phases. In contrast to the specimen attached with anode, the attacks were observed only at β phase with about 5 μm depth.

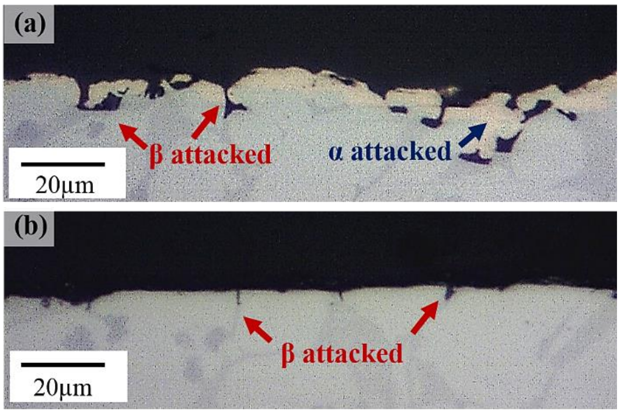

Fig. 9 Cross-sectional images of MAB (a) without- and (b) attached with sacrificial anode after anodically polarized from OCP to 1V. at a scan rate of 1 mV/S in 3.5% NaCl.

CONCLUSIONS

Thermally-sprayed aluminium coating and cathodic protection using aluminium sacrificial anode could protect MAB from deterioration more effective than polymer and aluminium bronze (Al-Cu) coatings. The effectiveness resulted from sacrificial property of aluminium coating that supply electron to protect MAB substrate and reduction of electrochemical potential of MAB to immunity state by sacrificial anode accordingly.

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Ms. Thunyaphorn Piankijsakul received B.E. (Materials Engineering) from King Mongkut's University of Technology Thonburi in 2012. She is studying M.E, Materials Technology at King Mongkut's University of Technology Thonburi. Her current interest is corrosion technology.

Dr. Napachat Tareelap received Ph.D (Metallurgy and Materials) in 2009. She is a lecturer at the Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi. Her current interests focus on corrosion, corrosion prevention and coating technology.

Dr.Nakorn Srisukhumbowornchai received Ph.D (Metallurgical Engineering) in 2003. He is a lecturer at the Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi. His current interests are materials characterization, metal forming and metal casting.

Ms. Kaysinee Sriruksasin received M.E. (Materials Technology) in 2006. She is a scientist at Research, Innovation and Partnerships Office, King Mongkut's University of Technology Thonburi. Her current interests include electro-deposition technique and materials characterization.