CORROSION RESISTANCE AND DURABILITY OF SILOXANE
CERAMIC/POLYMER FILMS FOR ALUMINUM ALLOYS
IN MARINE ENVIRONMENTS

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ABSTRACT

The objective of this study is to evaluate corrosion resistance and durability of siloxane ceramic/polymer films for aluminum alloys in marine environments.

Al5052-H3 and Al6061-T6 were selected as substrates, and HCLCoat11 and HCLCoat13 developed in the Hawaii Corrosion Laboratory were selected for the siloxane ceramic/polymer coatings. The HCLCoat11 is a quasi-ceramic coating that has little to no hydrocarbons in its structure. The HCLCoat13 is formulated to incorporate more hydrocarbons to improve adhesion to substrate surfaces with less active functionalities. In this study, two major corrosion evaluation methods were used, which were the polarization test and the immersion test.

The polarization tests provided theoretical corrosion rates (mg/dm²/day) of bare, HCLCoat11-coated, and HCLCoat13-coated aluminum alloys in aerated 3.15wt% sodium chloride solution. From these results, the HCLCoat13-coated Al5052-H3 was found to have the lowest corrosion rate which was 0.073mdd. The next lowest corrosion rate was 0.166mdd of the HCLCoat11-coated Al5052-H3. Corrosion initiation was found to occur at preexisting breaches (pores) in the films by optical microscopy and SEM analysis. The HCLCoat11 film had many preexisting breaches of 1-2µm in diameter, while the HCLCoat13 film had much fewer preexisting breaches of less than 1µm in diameter.

However, the immersion tests showed that the seawater immersion made HCLCoat13 film break away while the HCLCoat11 film did not apparently degrade, indicating that the HCLCoat11 film is more durable against seawater than the HCLCoat13. Raman spectroscopy revealed that there was some degradation of HCLCoat11 and HCLCoat13. For the HCLCoat11 film, the structure relaxation of Si-O-
Si linkages was observed. On the other hand, seawater generated C-H-S bonds in the HCLCoat13 film resulting in the degradation of the film. In addition, it was found that the HCLCoat11 coating had anti-fouling properties due to its high water contact angle.

As candidate materials for a marine construction (e.g. the heat exchangers for ocean thermal energy conversion (OTEC) plants), the HCLCoat11-coated Al5052-H3 proved to be a durable, corrosion resistant combination with anti-fouling characteristics.
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List of Abbreviations and Symbols

CCC: Chromate conversion coating

BR: bare

EC: Epoxy topcoat and CCC undercoated

ES: Epoxy topcoat and HCLCoat13 undercoated

PC: Polyurethane topcoat and CCC undercoated

PS: Polyurethane topcoat and HCLCoat13 undercoated

CP11: HCLCoat11-coated

CP13: HCLCoat13-coated

BR-5: bare Al5052-H3

EC-5: Epoxy topcoat and CCC undercoated Al5052-H3

ES-5: Epoxy topcoat and HCLCoat13 undercoated Al5052-H3

PC-5: Polyurethane topcoat and CCC undercoated Al5052-H3

PS-5: Polyurethane topcoat and HCLCoat13 undercoated Al5052-H3

CP11-5: HCLCoat11-coated Al5052-H3

CP13-5: HCLCoat13-coated Al5052-H3

BR-6: bare Al6061-T6

EC-6: Epoxy topcoat and CCC undercoated Al6061-T6

ES-6: Epoxy topcoat and HCLCoat13 undercoated Al6061-T6

PC-6: Polyurethane topcoat and CCC undercoated Al6061-T6

PS-6: Polyurethane topcoat and HCLCoat13 undercoated Al6061-T6

CP11-6: HCLCoat11-coated Al6061-T6

CP13-6: HCLCoat13-coated Al6061-T6
TS#1-1: Immersion Test Situation (Artificial seawater 141days immersion)
TS#1-2: Immersion Test Situation (Artificial seawater 243days immersion)
TS#2-1: Immersion Test Situation (Intertidal 132days immersion)
TS#2-2: Immersion Test Situation (Intertidal 224days immersion)
TS#3-1: Immersion Test Situation (Warm surface seawater 142days immersion)
TS#3-2: Immersion Test Situation (Warm surface seawater 204days immersion)
TS#4-1: Immersion Test Situation (Cold deep seawater 39days immersion)
1 INTRODUCTION

1.1 NATURE, BACKGROUND, AND SCOPE OF THIS STUDY

1.1.1 Metallurgy and Corrosion of Aluminum Alloy

Aluminum alloys are widely employed in aerospace, automotive, and maritime industries because of their low cost and useful properties; lightness, conductivity, strength, toughness, and corrosion resistance. Although pure aluminum has excellent corrosion resistance[1], its strength is too low and therefore must be alloyed with other metals to improve its mechanical properties. Some alloying elements such as copper, iron, and nickel can be more electrochemically noble than aluminum and can compromise its corrosion resistance, while other alloying elements such as manganese, magnesium, and silicon do not degrade corrosion resistance[1]. Wrought aluminum alloys that generally contain little or none of the deleterious alloying elements are the 3000 series (Al-Mn), the 5000 series (Al-Mg), and 6000 series (Al-Mg-Si). The corrosion potential of an aluminum alloy is determined by the solid solution. When the corrosion potential of the intermetallic compounds and precipitates is similar to that of the aluminum alloy, the corrosion resistance of these aluminum alloys is generally good. The corrosion resistance of the 3000 series (Al-Mn) aluminum alloy is good because the corrosion potential of MnAl₆ is very close to that of aluminum[1]. With regards to the 6000 series (Al-Mg-Si) aluminum alloy, while the precipitating of Mg₂Si strengthens the alloy, Mg₂Si weakens the corrosion resistance of the alloy because the corrosion potential of the intermetallic compounds of Mg₂Si is more active than that of the solid solution. The 6000 series aluminum alloy is not prone to stress corrosion and has a good resistance to atmospheric
corrosion[1]. The corrosion resistance of the 5000 series (Al-Mg) aluminum alloy is generally good. However, the amount of magnesium above the solid solubility limit lessens the corrosion resistance of the aluminum alloy due to the formation of Mg₂Al₃, which has a corrosion potential more negative to the alloy.

Precipitates and intermetallic compounds impede the forming of the oxide film and form a galvanic cell between precipitates and solid solution. Aluminum is prone to pitting corrosion in neutral media (especially if it contains halides), which basically covers all natural environments such as surface water, seawater, and moist air. The mechanism of pitting corrosion of an aluminum alloy in seawater is shown in Figure 1-1. Oxygen reduction at the cathode outside the pit such as an intermetallic compound occurs: \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \). Simultaneously, aluminum dissolves at the bottom of the pit, which is the anodic site: \( \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \) and the aluminum ions react with chloride ions: \( \text{Al}^{3+} + 4\text{Cl}^- \rightarrow \text{AlCl}_4^- \). Sequentially, \( \text{AlCl}_4^- + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ + 4\text{Cl}^- \) occurs and corrosion products, Al(OH)₃, deposit around a pit [2]. It is also reported that corrosion results in a uniform and continuous decrease in thickness over the entire surface area of aluminum when the pits have very small diameter on the order of a micrometer [1].

Both uniform and pitting corrosion of aluminum are greatly influenced by chloride ions. Chloride ions break down passivity of aluminum alloys. According to Revie and Uhlig[3], from the perspective of the oxide-film theory, chloride ion penetrates the oxide film through pores or defects easier than do other ions such as the sulfate ion. Alternatively, chloride ions may colloidally disperse the oxide film and increase its permeability. On the other hand, according to the adsorption theory, chloride ion adsorbs
on the metal surface in competition with dissolved oxygen or hydroxide ions. Once in contact with the metal surface, chloride favors hydration of metal ions and increases the ease with which metal ions enter into solution, opposite to the effect of adsorbed oxygen, which decreases the rate of metal dissolution[3].

![Figure 1-1 Mechanism of pitting corrosion on aluminum alloy](image)

### 1.1.2 Ocean Thermal Energy Conversion Plant

In tropical zones, the temperature difference of seawater at the surface (27 - 30°C) and at a depth of 1000m (4°C) is sufficient for use as the hot and cold reservoirs of a thermal engine. The concept of Ocean Thermal Energy Conversion (OTEC) was worked out in 1881. During the 1970s, the idea of producing electrical energy in tropical zones by means of OTEC was reconsidered in the United States, Japan and Europe. There are two approaches envisioned; open-circuit and closed circuit. In the open-circuit, surface water is evaporated and drives a turbine coupled with an alternator and is then condensed in contact with cold seawater pumped from a depth of 800 – 1000m. In the closed circuit, ammonia (NH₃) is used as the working fluid. In a exchanger, NH₃ evaporates in contact
with warm surface seawater, and after having driven the turbine, \( \text{NH}_3 \) condenses in another exchanger that is cooled by cold deep seawater [1].

The second approach requires two seawater-ammonia heat exchangers. Two potential materials for the heat exchangers are titanium and aluminum; although titanium has excellent corrosion resistance, its cost is generally considered to be prohibitive. A previous study on the OTEC project selected a few candidate aluminum alloys based on their mechanical strength, corrosion resistance, and cost[4]. The advantages of the 3000, 5000, and 6000 series aluminum alloys make them candidates for heat exchangers in Hawai‘i’s OTEC power plant; however, OTEC has some technical challenges that have impeded its implementation, including finding the best possible corrosion protection for the heat exchangers at an affordable cost.

1.1.3 Chromate Conversion Coating

Chromate conversion coatings, the industry standard, have been widely used for aluminum alloy corrosion protection. Chromate coating is composed of a continuous layer that consists of insoluble trivalent chromium compounds and soluble hexavalent chromium compounds[5]. The corrosion protection offered by the chromate conversion coating is basically two-fold: (1) it provides a thick and well attached barrier layer between the alloy and the electrolyte; (2) it acts as a self-healing material[6]. The self-healing mechanism can be described as follows: the coating layer consists of an amorphous and insoluble chromium oxide, with many hydroxyl groups where the formation of \( \text{Cr (III)}-\text{O-Cr (VI)} \) bonds can take place; these act as adsorption sites for chromate ions from the coating bath. The coating is therefore a mix of \( \text{Cr (III)}/\text{Cr (VI)} \) oxide. Where it is in contact with the electrolyte, the \( \text{Cr (VI)} \) migrates to the defects of
the layer, more vulnerable to corrosion attack. Then a series of reactions with the corrosion products, or with the walls of the defect can take place, leading to re-passivation.

As described above, chromate conversion coating has advantages for corrosion resistance. However, they will likely be banned by the United States Environmental Protection Agency due to their hazardous, carcinogenic hexavalent chromium salts. Thus, alternative chromate-free coatings are needed.

1.1.4 Siloxane Ceramic/Polymer Coating

Silicon is the most abundant metal in the earth’s crust, and evidence of silicate hydrolysis and condensation to form poly-silicate gels and particles is seen in many natural systems such as opal. The precious gem opal is composed of amorphous silica particles bonded together by lower-density silicate gels [7]. The essential ingredients required to form opals are an abundant supply of readily soluble silica and a source of water. Repeated hydrolysis and condensation steps involving the soluble silica lead to aqueous poly-silicate species that evolve into spherical particles of essentially anhydrous \( \text{SiO}_2 \) [8]. Manmade synthesis of poly-silicate gels from alkoxide precursors is known as “sol-gel” processing.

Generally, the sol-gel formation occurs in four stages: (1) hydrolysis, (2) condensation and polymerization of monomers to form chains and particles, (3) growth of the particles, (4) agglomeration of the polymer structures followed by the formation of networks that extend throughout the liquid medium resulting in thickening, which forms a gel [9].
Siloxane ceramic/polymer coatings, which consist of an inorganic silicon-oxygen backbone with organic side groups attached to silicon atoms (Figure 1-2) have recently drawn significant attention because they of their excellent corrosion resistance and their environmentally-friendly processing technique.

Figure 1-2Alkoxy-siloxane polymerization and bonding to Al surface

1.1.5 The Objectives of This Study

The Hawaii Corrosion Laboratory has been developing siloxane ceramic/polymer coatings which are proprietary. Although the chemical structures, mechanical properties, and formation parameters of these siloxane ceramic/polymer coatings have been investigated in previous studies in the Hawaii Corrosion Laboratory, there still remains to further study the corrosion barrier properties. The objective of this study is to evaluate the corrosion resistance and the durability of the siloxane ceramic/polymer film for Al5052-H3 and Al6061-T6 aluminum alloy substrates in marine environments. In addition, the performance will be compared against traditional coatings such as polyurethane, epoxy, and chromate conversion coating.

The result will help to determine candidate materials for a marine construction such as the heat exchangers of an OTEC plant.
1.2 LITERATURE REVIEW

1.2.1 Ceramic/Polymer Coating

Niemi[10] studied the efficacy of AdsilMicrogurad® AD95 as a corrosion abating coating on Al6061-T6 aluminum. AdsilMicrogurad® AD95 is an inorganic siloxane coating designed to protect bare stainless steel, aluminum, and copper from industrial chemical exposure, acid rain, salt spray coastal environments, and UV radiation. Experimentation with uncoated, coated, and coated-scribed specimens included the following: immersion for 3 months in ASTM simulated seawater, 0.5M sodium sulfate, and 3.15wt% sodium chloride; enclosure for 3 months in a high-humidity environment after being treated with the same electrolyte; outdoor exposure for up to 6 months at two different corrosive test sites; and potentiodynamic polarization experiments. Niemi reported that coated aluminum underwent no uniform corrosion during all of the experiments; however, accelerated crevice and pitting corrosion occurred when immersed in sodium chloride solution; on the other hand, bare coupons immersed in the same electrolytes corroded uniformly but underwent no crevice and pitting corrosion. Niemi also found that neither the bare nor the coated aluminum suffered crevice corrosion or pitting corrosion during immersion in ASTM simulated seawater.

Parkhill, Knobbe, and Donley[11] compared an epoxide-modified silicate sol-gel (i.e., SiO$_2$-epoxide ormosil spray) to bare aluminum treated with Alodine-1200 on Al2024-T3. Their research included microscopic analysis, potentiodynamic polarization, and a prohesion cabinet experiment. They found that the double layer epoxide ormosil coating was 2.2µm and provided a nearly impenetrable barrier to water and corrosive ions. The polarization test showed that the ormosil had several orders of magnitude better
corrosion protection than did Alodine-1200. The ormosil showed some signs of corrosion in a prohesion test after 168 hours of exposure; however, it was superior to the untreated and Alodine-1200 treated substrates.

Tiwari, Zhu, and Hihara[12] developed hybrid ceramic/polymer (ceramer) coatings for protecting aluminum alloy from corrosion, namelyHCLCoat3 and HCLCoat5. They used Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy to study the hardening process and bonding structure of their coatings. Their results indicate the presence of chemical bonding between the surface groups of metal substrate and the reactive functionalities in the coatings. They also conducted immersion experiments and electrochemical polarization tests. Bare and coated Al2024-T3, Al6061-T6, and Al7075-T6 aluminum alloys were immersed in Harrison’s solution for 30 days at room temperature. In addition, bare and coated Al6061-T6 aluminum alloy electrodes were polarized in aerated and deaerated of 0.5M sodium sulfate solution at two scanning rates: 0.1mV/s and 1.0mV/s. These results show that both HCLCoat3 and HCLCoat5 provide excellent corrosion protection to the metal substrate in open-circuit conditions. However, at a higher potential during anodic polarization testing, the anodic current densities of the coated electrodes approach and ultimately converged with that of the bare Al6061-T6 electrodes. Tiwari et al. concluded that either water permeating the coatings or the stripping of oxygen from the coating surface allowed the anodic current densities of the coated electrodes to approach and converge with that of the bare electrodes at a higher potential. The exact mechanism has not been identified.

Hihara et al.[13] studied the effectiveness of hydrogenated silicon, silicon nitride, silicon-carbon, and boron-doped silicon-carbon films on molybdenum and aluminum
substrates as corrosion barriers. In order to verify that the corrosion barrier of thin ceramic films compromised by defects in the films, they utilized polarization tests and exposure in a high-humidity environment. Scanning electron microscopy (SEM) revealed that corrosion occurred at pinholes caused by spallation, at micro-cracks, and at regions where SEM revealed no defects. The researchers also discovered that film integrity was dependent on the substrate. They concluded that in order to synthesize effective thin-film barrier coatings, the composition and intrinsic reactivity of the film, its mechanical and physical properties, and the compatibility between film and the substrate must be considered.

Castro et al.[14] studied the effectiveness of silica hybrid coatings deposited on AISI304 stainless steel by dipping and electrophoretic deposition (EPD). Their study investigated the protective behavior against corrosion of the coatings according to their thickness. Results from the potentiodynamic polarization in 0.6N NaCl revealed that the coatings that have a thickness of more than 2μm had lower current densities than did the bare stainless steel electrode.

Wang and Bierwagen [9] reviewed the recent developments and applications of sol-gel protective coatings on different metal substrates, such as steel, aluminum, copper, magnesium, and their alloys. Sol-gel is a good choice for a protective coating because its processing temperature is close to room temperature, which keeps thermal volatilization and degradation of entrapped species at a minimum. The study also includes a review of organic-inorganic hybrid sol-gel coatings on aluminum substrates. The researchers discovered three reasons that hybrid sol-gel coatings are much more popular than those that are pure inorganic oxide. First, hybrid coatings can easily form a thicker coat in the
micrometer scale range without cracks. Second, they have a lower curing temperature compared to the sintering of oxide layers. Finally, the hybrid sol-gel system more easily accepts anti-corrosion additives.

Planivel, Zhu, and Ooij[15] developed nano-particle-filled silane films, which offer excellent corrosion protection as well as paint adhesion to metals. Their nano-particle filled silane film was developed as follows: bis-sulfur silane was mixed with de-ionized water and ethanol by 5/5/90 vol% in order to convert the alkoxy (OR) groups of the silane to the active silanol(SiOH) groups. The solution was then stirred for 10 minutes and then aged in ambient conditions for at least 2 days. Silica nano-particles were added into the bis-sulfur silane solution. The concentrations of silica nano-particles in the silane solutions were 5, 15, 20, and 50 ppm. They conducted electrochemical tests and mechanical tests in order to examine the properties of the films. The tests showed that silane films, including silica between 5 and 15 ppm, improved corrosion resistance and that the film hardness increased as the amount of silica in the film did as well. They concluded that the appropriate amount of silica suppresses the cathodic reaction by reacting with the cathodically generated OH⁻ ions: SiO₂ + 2OH⁻ → SiO₂⁻⁻ + H₂O. The as-formed SiO₂⁻⁻ ions react with Al³⁺ ions at the anodes, forming a passive silicate film. Such cathodic inhibition was confirmed in the polarization test with a shift in Ecorr to lower values. Too much silica can make the silane film more porous as the silica particles adsorb silane.

Zhu and Ooij[16] developed a silane surface treatment based on the water soluble mixtures of bis-[trimethoxysilylpropyl]amine and vinyltriacetoxy silane (bis-aminosilane/VTAS mixture) with the aim of replacing the conventional chromate
processes in metal-finishing industries. They conducted corrosion tests ASTM B117 (salt spray test), ASTM 1654-92 (a corrosion test for painted or coated metals and alloys), ASTM B368 (a copper-accelerated acetic acid-salt spray test), a Machu test, a 9-month natural seawater immersion test, and Direct Current (DC)polarization tests with Al 2024-T3 and other alloys. These performance tests showed that water-based bis-aminosilane/VTAS mixtures provided comparable corrosion protection as well as paint adhesion for various metals, while chromates did not. It was concluded that two important contributors in the corrosion protection of Al2024-T3 by the bis-aminosilane/VTAS film are (1) good adhesion of the bis-aminosilane/VTAS mixtures to Al2024-T3 by the formation of Al0Si covalent bonds at the silane/metal interface and (2) water resistance or hydrophobicity of the silane film that prevents water intrusion into the interface between the silane film and the substrate.

1.2.2 Metallographic Method for Corrosion Investigation

To determine the cause of coating failure, Pan and Joseph[17] performed an investigation on three large hinged steel boxes (Boxes A, B, and C) whose coatings and paintings differed from one another. They used an optical microscope (OM) with a magnification ranging from 5 –100, an SEM equipped with an energy-dispersive X-ray spectroscopy (EDXA), and FTIR, all of which confirmed that Box B had a metallic layer of zinc and that none of the boxes had a galvanized zinc layer. The OM revealed extensive air bubbles in the primer, which significantly reduced the primer’s ability to withstand atmospheric moisture penetration. The EDXA spectrum of the contaminants revealed a strong chlorine peak, an indication that the boxes might have been exposed to a marine or coastal atmospheric environment. In order to explain the root cause of the
coating failure on Box B, they used FTIR analysis to analyze the chemical bonding and molecular structure of inorganic and organic compounds and discovered that all three topcoats on Box B were urethane-based. They also learned that the same type of primer was used on Boxes A and C. The difference was that Box B had a urethane alkyd primer.

Hatch’s book Aluminum: Properties and Physical Metallurgy explores the microstructure of aluminum alloys including OM, transmission electron microscopy replica methods (TEM), and SEM. Due to some disadvantages of TEM replica methods, such as (1) long specimen preparation time, (2) a selective specimen sampling plan because typical replicas must fit onto a 3mm grid, (3) artifacts in the replica that may occur during specimen preparation, and (4) unavailability of micro-chemical information for identification of chemical micro-heterogeneities, SEM was the preferred method.

Light microscopy is the major tool for micro-structural determination of aluminum alloys because it identifies most second-phase particles of sufficient size (>1µm), shows the size and distribution of resolvable particles, and reveals the grain or crystal structure of the aluminum or solid solution matrix. It can also reveal other features such as cladding thickness and diffusion, the type and depth of corrosive attack, and particles melting due to overheating. However, light microscopy does not reveal precipitate particles that are responsible for precipitation hardening, nor does it reveal dislocation arrangements.

Porosity, inclusions, and constituent particles—all of which are characteristic of the insoluble phase formed during solidification, are generally large enough to be measured optically. Features of this scale have strong effects on the fracture behavior of aluminum; especially fracture toughness, fatigue, and elongation. On the other hand,
features of a finer scale than constituent particles (e.g., dispersoids) are not generally measurable optically and must be measured using higher resolution techniques such as TEM or SEM. These smaller particles affect the re-crystallization behavior of aluminum alloys and also can directly or indirectly affect tensile properties.

1.2.3 Ocean Thermal Energy Conversion

Panchal et al.[4] conducted long-term fouling and corrosion research on aluminum alloys in order to determine which alloy would be most effective for heat exchangers of OTEC plants as a part of the United States Department of Energy’s Ocean Energy Technology (OET) program. They selected aluminum alloys because of their low cost and ductility. Given the mechanisms involved in OTEC, the researchers were especially interested in discovering the corrosion characteristics associated with surface (warm) water and deep-ocean (cold) water. Their data collection included wall-thickness loss, asymptotic corrosion rate, and long-term predictions of wall-thickness loss, corrosion pits, and corrosion-product film for bare Al3003 and Al5052 alloys. The OTEC program set an average wall thickness loss of 12.7μm/year for 30 years as a goal; such a rate would produce a wall-thickness loss of 380μm, but the acceptable depth of pits was set at 150μm. Since corrosion of aluminum occurs in two separate stages, the corrosion rates of aluminum alloys were evaluated in two stages For warm seawater, an asymptotic rate of corrosion of greater than 600μm/year was measured after 5 days of exposure to warm seawater, whereas after 200 days of exposure, the asymptotic corrosion rate dropped to a constant rate of less than 2μm/year. On the other hand, for cold water, the asymptotic rate of corrosion was 125μm/year after 5 days of exposure to cold seawater, and the maximum duration of the first stage corrosion was 100 days.
For the second stage, the corrosion rate was measured after 200 days at 5.4μm/year. There was no significant difference between the corrosion rates of the Al3003 and the Al5052 when exposed to warm seawater; in cold seawater, Al5052 had a lower uniform rate of corrosion than Al3003. However, the 30-year wall-loss thickness for Al3003 still was within engineering design limits set for OTEC applications. No localized corrosion or pitting was in the bare alloys in warm seawater, but infrequent and shallow corrosion or pitting was observed for both alloys.

The films on the aluminum alloys exposed to both warm and cold seawater were of similar thickness; however, the films differed in several important ways. The SEM view of a cross section of typical films formed in warm seawater showed a continuous film that appeared to be well attached to the metal surface; however, an SEM view of a cross section of typical films formed in cold seawater showed a discontinuous film that appeared to be less well-attached to the metal surface. In addition, the elemental compositions of the two films differed. The condenser film had a high concentration of silicon, and the warm-water films had a high concentration of magnesium.

1.2.4 Influence of Coatings and Intermetallic Compounds on Corrosion

He et al. [18] studied the chromate-based coating function by measuring the current flowing on chromated epoxy coated and non-chromated epoxy coated steel and aluminum (Al2024-T3) substrates. They reported that both the steel and aluminum substrates coated with chromated epoxy exhibited a significant delay before the onset of corrosion within a scribe, compared with the substrates coated with non-chromated epoxy due to cathodic inhibition of \( \text{CrO}_4^{2-} \). The current density maps for steel suggest that the reduction reaction might occur at the surface of chromated epoxy coating.
Hu, Zhang, and Cao[19] proposed the time-dependent impedance model of epoxy coated aluminum alloy during exposure to 3.5wt% sodium chloride solution. According to the paper, after water and oxygen reached the base, the impedance associated with corrosion of the alloy base changed with the immersion time as follows. Initially there is an active corrosion period (double layer capacitance, $C_{dl}$, in parallel to the charge transfer resistance of electrochemical corrosion $R_{ct}$), which is followed by an obstruction in the diffusion of corrosion production at the intermediate period as a result of the presence of coated film (a constant phase element $Z_{diff}$ was additionally in series with $R_{ct}$), and the appearance of impedance related to a chlorine ion incorporating reaction with the alloy base. They concluded that water and oxygen diffuses quickly through the epoxy coating while chloride ions do not.

Using SEM, auger electron spectrometer (AES), and energy dispersive X-ray analysis (EDXA), Grilli, Baker, Castle, Dunn, and Watts[6] investigated the formation of a chromate conversion coating at intermetallic compounds sites of Al2219 alloy as well as the corrosion initiation at these sites in 3.15wt% sodium chloride solution. They found that the coating was thinner and more defective on the intermetallic compounds. Chloride attacked the intermetallic compounds, a response that led to being preferentially dissolved and $\text{Al(OH)}_3$ being deposited on and around intermetallic compounds. In addition to $\text{Al(OH)}_3$, a very thin layer of iron and manganese oxides as well as elemental copper precipitates were deposited onto the intermetallic compounds and surrounding areas as corrosion products. The ALODINE coating offered stronger resistance to the corrosive attack of intermetallic compounds particles in 3.5wt% sodium chloride solution than did the untreated surface.
Keene et al.[20] investigated failure pathways of a dual layer coating system consisting of polyurethane topcoats and epoxy primers applied to Al2024-T3 substrates pretreated with chromate conversion coating. Epoxy resins are known for their excellent adhesion as well as their resistance to chemical attack and heat. The commercial aluminum-copper alloy Al2024-T3 on which these coatings are applied contains several alloying elements that lead to the formation of a complex, multiphase structure. The intermetallic compounds Al$_2$Cu, Al$_2$CuMg, Al$_2$Cu$_2$Fe, Al$_7$Cu$_2$Fe, Al$_{12}$Si(FeMn)$_3$, Al$_{20}$Cu$_2$(MnFe)$_3$, (Al,Cu)$_6$Mn, and Al$_{20}$Cu$_3$Mn$_3$ are on the alloy surface; they provide local conductivity due to the thinner oxide layer. Keene et al. concluded that there are two failure pathways: failure to control the polydispersity of the bisphenol-A component of the epoxy coating during its manufacture, and copper in the Al2024-T3 prevented the chromate conversion coating from achieving target thickness.

Grilli et al.[2] investigated the role of intermetallic compounds in pitting corrosion of Al2219 alloy. In this paper, second phase particles were characterized by AES, scanning acoustic microscopy (SAM) and EDXA. The Al-Cu-Fe-Mn second phase particles were found to act as pitting initiation sites, indicating they were cathodic with respect to the Al alloy matrix, and the pitting attack was concentrated at the aluminum matrix adjacent to the intermetallic compounds.

1.3 METHODS

Test methods and materials were chosen according to findings from the literature review. There are two common tests for evaluating corrosion on materials protected by coatings: the polarization test and the immersion test. The polarization test reveals the anodic dissolution characteristics and the cathodic reaction kinetics. Although the
polarization test can provide fundamental information about dissolution characteristics and reaction kinetics under very well-controlled conditions, it is difficult to determine actual corrosion behavior and film degradation from the results of the polarization tests. Thus, the immersion test is needed to demonstrate the degree to which siloxane ceramic/polymer coatings mitigate corrosion on aluminum alloys in simulated as well as actual marine environments.

In this study, Al5052-H3 and Al6061-T6 were selected as substrate alloys. For the siloxane ceramic/polymer coatings, the HCLCoat11 and HCLCoat13 developed in the Hawai‘i Corrosion Laboratory were selected. The HCLCoat11 is a quasi-ceramic coating that has little to no hydrocarbons in its structure. The HCLCoat13 is formulated to incorporate more hydrocarbons to improve adhesion to substrate surfaces with less active functionalities.

In the polarization test, 0.5M sodium sulfate solution and 3.15wt% sodium chloride solution were used. Six types of electrodes were studied: bare Al5052-H3 (BR-5), HCLCoat11-coated Al5052-H3 (CP11-5), HCLCoat13-coated Al5052-H3 (CP13-5), bare Al6061-T6 (BR-6), HCLCoat11-coated Al6061-T6 (CP11-6), and HCLCoat13-coated Al6061-T6 (CP13-6).

The immersion test examined double coating schemes in addition to single siloxane ceramic/polymer coatings. Six coating schemes were evaluated for the immersion test: HCLCoat11 single coating (CP11), HCLCoat13 single coating (CP13), epoxy top coating/chromate conversion primary coating (EC), polyurethane top coating/chromate conversion coating (PC), epoxy top coatings/HCLCoat13 primary coating (ES), and polyurethane top coating/HCLCoat13 primary coating (PS). The
corrosion protection of these coatings was evaluated by mass change rate of coupons and surface damage analysis.

After polarization and immersion tests, changes in the surface chemistry and topography were investigated by optical microscopy, scanning electron microscopy, and Raman spectroscopy.

1.4 PRINCIPAL RESULTS OF TESTS

The anodic polarization test showed that there was no significantly difference in the corrosion potential among BR, CP11, and CP13 electrodes. Although all electrodes showed passivity in 0.5M sodium sulfate solution, pitting corrosion occurred at between -0.6 and -0.7V vs SCE on the BR, CP11, and CP13 electrodes in 3.15wt% sodium chloride solution. Cathodic polarization test showed that the oxygen reduction and hydrogen evolution occurred on all electrodes. The current density of CP11 electrode was smaller than that of BR electrode by one order of magnitude and the current density of CP13 electrode was smaller than that of CP11 electrode by one order of magnitude. Moreover, the morphological change investigation of cathodic-polarized electrodes showed cathodic corrosion occurred.

For the immersion tests, visual results showed that EC and PC coupons had excellent corrosion resistance; the next best was a CP11 coupon; ES and PS had severe corrosion and the organic coating delaminated. The results of the areal mass change rates of immersion test coupons showed that the rate of the CP11 coupons were small, indicating that the film degradation and macrofouling were small. The morphological change investigation of immersion test coupons showed that different corrosion behavior at the open-circuit potential for each coating scheme: for BR coupons, pitting corrosion
occurred and semitransparent scale covered on surface; cathodic corrosion occurred on CP11 coupons; with regard to CP13 coupons, the film broke away and pitting corrosion occurred on the exposed substrate.

1.5 PRINCIPAL DISCUSSION

Pitting corrosion occurred on both CP11 and CP13 electrodes at approximately the same potential as the BR electrode, indicating that chloride ions reached the substrates through the siloxane ceramic/polymer films. There are three plausible explanations for why pitting corrosion occurred on the coated electrodes in 3.15wt% sodium chloride solution; (1) film break down by applied electric field during polarization tests, (2) anodic current emanating from preexisting breaches, and (3) chloride ions penetration through the film by diffusion and migration. The dielectric strength of the films was enough to resist breakdown by the applied electric field; therefore, the first postulate can be denied. Also, the diffusion and migration speed of chloride ions are too slow; thus, the third postulate can be denied. SEM investigation revealed that the HCLCoat11 film had many preexisting breaches whose diameters were 1-2µm, and the HCLCoat13 film had a much lower density of preexisting breaches, whose diameters were less than 1µm. From this investigation, it is concluded that chloride ions can penetrate the films through the breaches and initiate pitting. During cathodic polarization, cathodic corrosion occurred on BR, CP11, and CP13 electrodes. The electrolyte penetrated the films at the preexisting breaches during cathodic polarized.

From the results of the polarization tests, the corrosion rate of BR-5, BR-6, CP11-5, CP11-6, CP13-5, and CP13-6 was determined. From these results, the HCLCoat13-
coated Al5052-H3 was found to have the lowest corrosion rate which was 0.073mdd. The next lowest corrosion rate was 0.166mdd of the HCLCoat11-coated Al5052-H3.

In immersion tests, the HCLCoat11 film did not apparently degrade; on the other hand, the HCLCoat13 film crazed and delaminated. Raman spectroscopy revealed that the HCLCoat11 film was degraded due to the structure relaxation of Si-O-Si linkages. Raman spectroscopy also revealed that C-H-S bonds formed in the HCLCoat13 film during seawater immersion. The degradation of the HCLCoat13 could be due to the C-H-S bond formation by the seawater immersion.

In order to evaluate the films as an antifouling coating, the fouling rate was determined from the warm surface seawater immersion test coupons. The best fouling rate was 99.84% for a CP11 coupon; the worst fouling rate was 27.51% for a PC coupon. The HCLCoat11 coating has a better fouling release function compared to other siloxane coatings.

1.6 PRINCIPAL CONCLUSIONS
The siloxane ceramic/polymer coatings (HCLCoat11 and HCLCoat13) developed in the Hawaii Corrosion Laboratory can be concluded having excellent corrosion resistance in marine environments.

The HCLCoat11 film has preexisting breaches (pores) whose diameter is 1-2µm, resulting in cathodic corrosion at the breaches at open-circuit potential; however, the obvious film degradation does not occur in seawater. Also, the HCLCoat11 film has the excellent anti-fouling properties.

The HCLCoat13 film has almost no preexisting breaches. Even if there is preexisting breach, the diameter of it is less than 1µm. This results in HCLCoat13 film
having better short-term corrosion resistance than the HCLCoat11 film by several percent in the polarization tests; however, for immersion tests longer than one month, HCLCoat11 performed much better than HCLCoat13, which delaminated from the substrate.

The best results were obtained with the HCLCoat11-coated Al5052-H3. These specimens had excellent combination of low corrosion rates and anti-fouling characteristics, which would make it a good candidate for the exchangers in OTEC systems.
2 MATERIAL SELECTION

2.1 ALUMINUM ALLOY SELECTION

Because Panchal et al.[4] found that wrought Al5052 has good seawater corrosion resistance, it was selected as one of the aluminum alloy substrates. As mentioned in the previous chapter, the wrought 5000 series is a strain hardening alloy that has excellent corrosion resistance. Al5052-H3 consists of 2.2wt% magnesium, 0.15wt% chromium, and a remainder of aluminum[1]. The H3 condition, which indicates that the alloy is strain hardened and stabilized by a low-temperature heat treatment or by heating introduced during fabrication, is used to produce stable properties with higher elongation levels and improved forming characteristics[21].

In addition to Al5052-H3, Al6061-T6 was also selected for the substrate alloy of this study because of its relatively good corrosion resistance and good performance with the ceramic/polymer coating[22]. The wrought 6000 series is an age hardening alloy. The composition of Al6061-T6 is 0.8wt% magnesium, 0.4wt%silicon,0.15wt% copper, 0.04wt% chromium, and a remainder of aluminum[1].The T6 temper indicates that the solution is heat treated and artificially aged.

2.2 CHROMATE CONVERSION COATING (CCC)

In order to compare the performance of the ceramic/polymer coatings to that of an industry standard, chromate conversion coatings were also evaluated. ALODINE 1201 was selected for the comparison due to its good adhesion to aluminum alloy substrates and excellent corrosion resistance [2, 6, 23]. ALODINE 1201 is nonflammable and chromic acid-based. The coating it forms becomes an integral part of the aluminum surface and is gold to tan in color.
2.3 CERAMIC/POLYMER COATING

The Hawai‘i Corrosion Laboratory developed and evaluated novel ceramic/polymer coatings [12, 22]. In this study, HCLCoat11 and HCLCoat13 coatings were examined. The HCLCoat11 coating is a quasi-ceramic coating that has little to no hydrocarbons in its structure. The HCLCoat13 coating is formulated to incorporate more hydrocarbons to improve adhesion to the surfaces with less active functionalities.

2.4 ORGANIC COATING SELECTION

For the immersion test, two organic top-coatings were selected: polyamide-cured epoxy coating and polyurethane coating.

2.4.1 Epoxy

The epoxy coating was a polymer of epichlorohydrin and bisphenol A called D.E.R. 331 (Dow Chemical, USA) and a curing agent called Ancamide 2325 (Air Products, USA). This epoxy resin and curing agent are widely used for aluminum alloy coatings; their formulation is reviewed in a few papers [18, 24].

2.4.2 Polyurethane

Two polyurethane coatings were used. The first was a two-part, water-borne linear polyurethane enamel called WR-LPU Urethane Topcoat (System Three, USA). This polyurethane coating is widely used in marine environments. The second was a two-component, solvent-based polyurethane called CONATHNE CE-1155 (CYTEC, USA). The CONATHNE CE-1155 provides outstanding resistance and good abrasion resistance and is qualified to MIL-I-46058.
3 METHOD OF POLARIZATION TEST

3.1 PROCEDURES OF MAKING ELECTRODES

The following sections describe the making of a typical electrode as seen in Figure 3-1.

3.1.1 Bare Electrode

An electrode coupon was cut in 1.0cm by 1.0cm from an aluminum alloy strip. The cuts were made using a Buehler Isomet low speed saw with a Buehler diamond wafer blade (series 15 LC diamond). Corners of the electrode coupon were filleted by wet grinding on a Buehler Ecomet 6 variable speed grinder-polisher using Buehler-Met II silicon carbide 180-grit grinding paper. The electrode coupon was attached with copper wire by silver conductive epoxy (MG Chemicals). The electrode coupon attached with copper was hardened at 70˚C for 20 minutes in an oven. About 20cm of borosilicate glass tubing was made by scribing and breaking it from a longer section. To dull the edges, the
ends of the glass tube were heated to a molten state with a gas torch and then allowed to cool. The copper wire was inserted into the tube until the aluminum electrode coupon was almost touching the tubing. A clear epoxy patch adhesive was used to attach the aluminum and copper to the end of the tubing. Care was taken to ensure that the tubing end was sealed with epoxy, that no copper was exposed, and that only one face of the aluminum electrode coupon was exposed. The epoxy was cured in the oven at 70˚C for 1.5 hours and then removed and allowed to cool to room temperature. The exposed face of the aluminum electrode coupon was wet ground using Buehler Ecomet 6 variable speed grinder-polisher at three levels: 180-grit, 320-grit, and 600-grit. All of the grinding papers used were Buehler-Met II silicon carbide grinding paper. After grinding with 600-grit paper, the electrode coupon surface was rinsed with purified water. Polishing was done on a Buehler Ecomet 6 variable speed grinder-polisher at 1µm and 0.3µm using Buehler Micropolish II compounds; the 1µm and 0.3µm compounds were deagglomerated alpha alumina. After polishing, the electrode coupon surface was rinsed with purified water and blown dry with compressed air. The electrodes were stored in a dry box right before the polarization test.

The bare Al5052-H3 electrode is abbreviated to BR-5 electrode, and the bare Al6061-T6 electrode is also abbreviated to BR-6 electrode.

3.1.2 Coated Electrode

In order to investigate the electrochemical properties of HCLCoat11 and HCLCoat13 coated aluminum alloy substrates, HCLCoat11 and HCLCoat13 coated electrodes were made. The bare electrodes were used for making coated electrodes. The bare electrode was dipped into HCLCoat11 or HCLCoat13 for 10 seconds. The coated
The electrode was then dried at room temperature of 25 °C for 2 days and in an oven at 37 °C for 1 night.

The HCLCoat11-coated Al5052-H3 and Al6061-T6 electrode is abbreviated to CP11-5 electrode and CP11-6 electrode, respectively. Similarly to the HCLCoat11-coated electrode, the HCLCoat13-coated Al5052-H3 and Al6061-T6 electrode is abbreviated to CP13-5 electrode and CP13-6 electrode, respectively.

3.2 PROCEDURES OF POLARIZATION TEST

3.2.1 Electrolyte Preparation

One half molar sodium sulfate and 3.15wt% sodium chloride were prepared with purified water and Fisher Scientific Certified A.C.S. sodium sulfate and sodium chloride, respectively. Their initial pH was approximately 7.

3.2.2 Polarization Procedure

Deaerated electrolytes were sparged with compressed nitrogen and aerated electrolytes were sparged with compressed air. Before the experiments, electrodes were put in purified water for 10 minutes to make the surface condition of all electrodes the same. During the experiments, the electrolytes were kept at a constant temperature of 25.5°C. A three-electrode electrolytic cell with platinum counter electrode and saturated Calomel reference electrode was used.

The open-circuit potential was measured for a 1-hour period using a Potentiostat/Galvanostat Model 273(Princeton Applied Research). Subsequently, potentiodynamic polarization was performed using a Potentiostat/Galvanostat Model 273.
at a scan rate of 1mV/s. The potential and current were recorded using Electrochemistry PowerCORR software (Princeton Applied Research) on a Windows system.

The reported polarization curve was an average of three polarization curves conducted at the same test conditions. For example, the curve was made by taking the mean of the logarithms of the current densities of the three experiments performed on electrodes in electrolyte solution at each voltage step in the polarization scan. Each side of an error bar corresponds to one standard deviation from the mean for the three current densities at that potential.

### 3.2.3 Morphological Change Investigation

Metallographic observation of electrodes from the polarization tests allows us to study the morphological changes caused by both the anodic or cathodic reactions. Identifying morphological changes on immersion coupons with those on the electrodes would provide clues for elucidating corrosion initiation. Thus, morphological change of the surface of polarized electrodes was investigated with optical microscopy and scanning electron microscopy (SEM) in concert with energy dispersive X-ray analysis (EDX). The scanning electron microscope used in this study was the Hitachi S-3400 SEM and the energy dispersive X-ray spectrometer was the Oxford Instruments INCA X-sight (model 7021).
4 METHOD OF IMMERSION TEST

4.1 IMMERSION TEST

In order to evaluate the effectiveness of the siloxane ceramic/polymer coating against corrosion in the marine environment, as shown in Figure 4-1, two single coat and four two-coat schemes and bare coupons were tested: HCLCoat11 (single coat), HCLCoat13 (single coat), epoxy topcoat and HCLCoat13 undercoat (two-coat), polyurethane top coat and HCLCoat13 undercoat (two-coat), epoxy topcoat and chromate conversion undercoat treatment (two-coat), and polyurethane top coat and chromate conversion undercoat treatment (two-coat).

![Figure 4-1 Coating Schemes](image-url)

The coated and bare coupons were made using the procedure shown in section 5.1. The coupons were immersed in artificial seawater at the Hawai‘i Corrosion laboratory and natural seawater immersion at three field test sites for about 120 days and about 240 days. The total number of coupons was 156 x 2 substrates x 2 test periods for a total of
624 coupons. In order to compare corrosion damage after immersion, weight loss measurement and quantitative surface damage analysis were performed.

4.2 PROCEDURES OF MAKING COUPONS

4.2.1 Manufacturing of Coupons

Test coupons were manufactured in the College of Engineering machining shop at the University of Hawai‘i at Mānoa. Figure 4-2 shows the shape and size of the coupons.

Manufacturing the aluminum coupons for this study involved the following steps:

(1) Sheets of Al5052-H3 and Al6061-T6 measuring 72 x 48 inches were cut with a hydraulic shear into 2.125 inch x 48 inch strips. (2) The strips were ground with a 180-grit aluminum oxide grinding paper attached to a finishing sander. (3) Then, the strips were sheared into 2.125 inch by 1.125 inch coupons. (4) To remove the sheared regions of the coupons, the coupons were milled to a 2 inch x 1 inch shape.

4.2.2 Surface Preparation of Coupons

Surface preparation is required to improve coating adhesion. In order to remove oils, greases, soil salts, and other contaminants, a non-flammable phosphoric acid based
cleaner ALUMIPREP 33 (Henkel, USA) was used. The surface preparation involved the following steps: ALUMIPREP 33 was diluted with purified water in 25 parts ALUMIPREP 33 and 75 parts water. Then coupons were dipped in the dilute ALUMIPREP 33 solution for 2 minutes—each side for 1 minute. The coupons were then rinsed with water and then, cleaned in an ultrasonic cleaner for 5 minutes. Finally, the coupons were rinsed with purified water, dried with a paper towel, and then wiped with ethanol. The procedure is shown in Figure 4-3.

![Procedure of surface preparation](image)

**Figure 4-3 Procedure of surface preparation**

### 4.2.3 Chromate Conversion Coating

After surface preparation by ALUMIPREP 33, 192 coupons were treated with the chromate conversion coating for EC and PC coupons. The chromate conversion coating was applied as follows: ALODINE 1201 was diluted with purified water in 25 parts ALODINE 1201 and 75 parts purified water. Coupons were then dipped for 3 minutes after which they coupons were rinsed with purified water and then dried on tissue paper. The procedure is shown in Figure 4-4.
4.2.4 Ceramic/Polymer Coating: HCLCoat11 and HCLCoat13

Ninety six coupons were coated with HCLCoat11 for CP11 coupons and 288 coupons were coated with HCLCoat13 for ES, PS, and CP13 coupons. Both coating procedures are described follows: A coupon was dipped in either HCLCoat11 or HCLCoat13 for 10 seconds after which the coupon was dried at room temperature (25 °C) for 48 hours and subsequently in an oven at 37 °C for 12 hours. The procedure is shown in Figure 4-5.

![Figure 4-4 Procedure of chromate conversion coating](image-url)
4.2.5 Epoxy Coating

The epoxy coating batch was composed of epoxy resin (D.E.R. 331): curing agent (Ancamide 2325): solvent (MEK) of 5:3:5 by weight. After the chromate conversion coating or the HCLCoat13 coating was applied to coupons, the epoxy coating was applied in following steps for EC and ES coupons: The pre-coated coupons were dipped in the epoxy for 10 seconds and then hung on a rack. Subsequently, the coupons were cured at 35 °C in an oven for 24 hours.

4.2.6 Polyurethane Coating

For chromate conversion coated coupons, the water-borne polyurethane WR-LPU polyurethane topcoat was used for the PC coupons. The solvent-based polyurethane CONATHNE CE-1155 was used for PS coupons. The solvent-based topcoat was used for the PS coupons since they repelled the water-based topcoat.

To coat the coupons, they were dipped in polyurethane for 10 seconds and then dried at room temperature (25 °C) for 96 hours.
4.3 PROCEDURE OF IMMERSION TESTS

All coupons excluding the bare coupons were scribed as shown in Figure 4-6.

![Diagram of scribe on coupon]

Figure 4-6 Size of scribe on a coupon

All coated coupons prior to immersion are shown below.

![Images of coated coupons]

Figure 4-7 Back (no scribe) side of Al5052-H3 coupons before immersion

![Images of coated coupons with scribe]

Figure 4-8 Front (1” scribe) side of Al5052-H3 coupons before immersion
4.3.1 Artificial Seawater Immersion

The artificial ASTM seawater immersion test setup is shown in Figure 4-11. The temperature of the artificial seawater was sustained at 30°C using a heater and a water circulation pump. Each beaker was filled with artificial ASTM seawater while water was circulated around the beakers to maintain the temperature at 30°C.
4.3.2 Intertidal Immersion

The coupon racks were mounted on a concrete bridge at Coconut Island as shown in Figure 4-12. The coupon racks were exposed to the atmosphere at low tide and were fully immersed at high tide. There are two high and low tide cycles per day. This splash-spray zone is known to be more corrosive than continuous immersion.

These coupon racks were photographed approximately once per month in order to monitor the growth of marine organisms or corrosion progress.

4.3.3 Warm Surface Seawater Immersion

The coupon racks were mounted as shown in Figure 4-13. The coupon racks were continuously immersed in the warm seawater at Coconut Island.

The water at Coconut Island is generally calm and many marine organisms such as algae, corals, barnacles, sea cucumbers, and fish thrive in this site. In order to monitor
the propagation of marine growth on the coupons, the coupon racks were brought to the surface approximately once per month and also photographed.

![Figure 4-13 Warm surface seawater immersion test](image)

4.3.4 Cold Deep Seawater Immersion

Figure 4-14 shows the test chamber. The two test chambers were set up at a Kona test site at Makai Ocean Engineering, Inc. on the Big Island. The cold deep seawater was pumped up from a depth of 674m deep. The temperature and the amount of dissolved oxygen approximately were 8°C and 1.4ppm, respectively.
4.4 METHODS OF DAMAGE EVALUATION

4.4.1 Initial Coupon Cleaning

Coupons that were immediately removed from the immersion racks or coupon holders showed some depositions on the surfaces. Also, for the coupons removed from field test sites, marine organisms such as algae thrived on the coupon racks. In order to remove the precipitates and marine organisms attached to the surface of coupons, an initial coupon cleaning was conducted: coupons were cleaned with tap water in a bucket several times. After the cleaning with tap water, the coupons were immersed for 60 minutes in an ultrasonic cleaner and dried at room temperature for 1 day.
4.4.2 Areal Mass Change Rate

The rate of mass change per exposed area of the coupons after the immersion test was investigated with measuring the weight of the coupon after the initial coupon cleaning. During the immersion tests, the coupons gained mass by three mechanisms: production of adherent corrosion product and/or deposition of products from the electrolyte on the coupons, and/or growth of marine organisms on the coupons. The coupons lost mass by two mechanisms: spallation or delamination (if they were coated) and/or pitting or crevice corrosion so severe that the corrosion product is in copious quantities and non-adherent. In the results of this investigation, “gain” and “losses” in mass are net gains and net losses. A gain does not mean that the coupon did not lose mass; it simply means that the net mass change was a gain. The gains are reflected as positive areal mass change rate and losses are negative.

Corrosion products could be removed with a conventional cleaning procedure for the bare coupons. Thus, in order to know actual corrosion rates of aluminum alloys, two out of three bare coupons were conducted with the conventional cleaning procedure. The cleaning procedure was as follows: coupons were immersed in the cleaning solution at 90°C which was made from phosphoric acid (50mL), tri-oxide chromium (20g), and reagent-grade water to make 1000mL[25]. After immersed for 5 minutes, the coupons were rinsed with tapped water and in ultrasonic cleaner for 10 minutes, and wiped with a paper towel.

After the initial coupon cleaning and/or the conventional cleaning procedure, the weight measurement was conducted with a 0.0001g precision on a METTLER TOLEDO analytical balance.
4.4.3 Metallographic Investigation

Similar to the morphological-change investigation of polarized electrodes, the morphological change of the immersion test coupons (BR, CP11, and CP13 coupons) were also investigated with optical microscopy. This investigation provided us with key information about corrosion initiation on bare and coated aluminum alloys.

Moreover, in order to evaluate the surface damage of the coupons, the areal analysis[26] was used for the optical microscopy images. After capturing an image of the coupon surface with an optical microscope, the image was post processed using MATLAB R2011a (MathWorks). The areal analysis procedure was conducted[27]: (1) The MATLAB function “graythresh” computed a threshold that can be used to convert an intensity image to a binary image. (2) In order to distinguish damage areas, the threshold was adjusted in the range between 0 and 1. (3) The MATLAB function “im2bw” converted the colored or grayscale image into a black-white image with the adjusted threshold value. (4) The MATLAB function “bwarea” provided a damage area. (5) Area fraction was determined by dividing the damage area by total area.
5 RESULTS OF POLARIZATION TEST

5.1 OPEN-CIRCUIT POTENTIAL

An open-circuit potential (OPC) was measured for a 1-hour period in order to stabilize the open-circuit potential of the electrode immersed in the electrolyte before anodic and cathodic polarization tests.

5.1.1 0.5M Sodium Sulfate Solution

The open-circuit potentials in aerated and deaerated 0.5M sodium sulfate solution are shown in Table 5-1 and Table 5-2. Although the open-circuit potentials were different from bare and the siloxane ceramic/polymer coated electrodes, it was difficult to conclude that the HCLCoat11 and HCLCoat13 films affect the open-circuit potential in sodium sulfate solutions.

Table 5-1 Open-circuit potentials in deaerated electrolyte

<table>
<thead>
<tr>
<th></th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>-1.094</td>
<td>-1.032</td>
<td>-1.032</td>
<td>-1.089</td>
<td>-1.159</td>
<td>-1.090</td>
</tr>
<tr>
<td>[V vs SCE]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5-2 Open-circuit potentials in aerated electrolyte

<table>
<thead>
<tr>
<th></th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>-0.671</td>
<td>-0.583</td>
<td>-0.613</td>
<td>-0.620</td>
<td>-0.717</td>
<td>-0.634</td>
</tr>
<tr>
<td>[V vs SCE]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.1.2 3.15wt% Sodium Chloride Solution

The open-circuit potentials in aerated and deaerated 3.15wt% sodium chloride solution are shown in Table 5-3 and Table 5-4. Similarly to 0.5M sodium sulfate solutions, the open-circuit potentials were different for the bare and the siloxane ceramic/polymer
coated electrodes, and it was difficult to conclude that the HCLCoat11 and HCLCoat13 films affect the open-circuit potential in sodium chloride solutions.

Table 5-3 Open-circuit potentials in deaerated electrolyte

<table>
<thead>
<tr>
<th></th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC [V vs SCE]</td>
<td>-0.949</td>
<td>-0.975</td>
<td>-1.063</td>
<td>-1.061</td>
<td>-1.044</td>
<td>-1.144</td>
</tr>
</tbody>
</table>

Table 5-4 Open-circuit potentials in aerated electrolyte

<table>
<thead>
<tr>
<th></th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC [V vs SCE]</td>
<td>-0.757</td>
<td>-0.789</td>
<td>-0.778</td>
<td>-0.739</td>
<td>-0.753</td>
<td>-0.735</td>
</tr>
</tbody>
</table>

5.2 ANODIC POLARIZATION

5.2.1 0.5M Sodium Sulfate Solution

Anodic polarization diagrams in 0.5M sodium sulfate solution for BR-5, CP11-5, and CP13-5 electrodes are compared in Figure 5-1 and Figure 5-2.

In the deaerated 0.5M sodium sulfate solution (Figure 5-1), the curve of the BR-5 electrode showed passivation by Al₂O₃ layer. The curves of CP11-5 and CP13-5 (Figure 5-1) were also influenced by the passivation. The current density of CP13-5 was less than that of CP11-5; moreover, the current density of CP11-5 was always less than that of BR-5 (Figure 5-1).
Figure 5-1 Anodic polarization diagrams of BR-5, CP11-5, and CP13-5 electrodes in deaerated 0.5M sodium sulfate solution.

Figure 5-2 Anodic polarization diagrams of BR-5, CP11-5, and CP13-5 electrodes in aerated 0.5M sodium sulfate solution.
The polarization behavior in aerated 0.5M sodium sulfate solution (Figure 5-2) varied from that in deaerated 0.5M sodium sulfate solution (Figure 5-1). The curve of BR-5 showed typical passivation behavior; whereas, the curves of CP11-5 and CP13-5 showed increasing anodic currents with increasing polarization. However, since the anodic current densities of CP11-5 and CP13-5 were lower than that of BR-5, the coated electrodes were still considered to be passivated.

Anodic polarization diagrams in 0.5M sodium sulfate solution for BR-6, CP11-6, and CP13-6 electrodes are compared in Figure 5-3 and Figure 5-4.

![Anodic polarization diagrams of BR-6, CP11-6, and CP13-6 electrodes in deaerated 0.5M sodium sulfate solution](image)

The BR-6 displayed passivation similar to that of bare Al5052-H3. The CP11-6 and CP13-6 were also passivated as their current densities were less than that of BR-6. The current density of the CP13-6 was less than that of the CP11-6 near the open-circuit
potential; moreover, the current density of the CP11-6 was less than that of the BR-6 near the open-circuit potential.

Figure 5-4: Anodic polarization diagrams of Al6061-T6 electrodes in aerated 0.5M sodium sulfate solution: bare, HCLCoat11-coated, and HCLCoat13-coated

The curves of the CP11-6 and CP13-6 were same as the curve of the BR-6 (Figure 5-4). This result indicated that the coatings of these electrodes may have been thinner.

The Figure 5-5 and Figure 5-6 show the comparison of BR-5 and BR-6 in anodic polarization in 0.5M sodium sulfate solution.
Figure 5-5 Comparison of anodic polarization diagrams of BR-5 and BR-6 in deaerated 0.5M sodium sulfate solution

Figure 5-6 Comparison of anodic polarization diagrams of BR-5 and BR-6 in aerated 0.5M sodium sulfate solution
Both BR-5 and BR-6 showed the passivity in both aerated and deaerated 0.5M sodium sulfate solutions. The current density of the BR-5 was less than that of the BR-6 near the open-circuit potential, indicating that anodic dissolution would occur more preferably on Al6061-T6 than on Al5052-H3.

5.2.2 3.15wt% Sodium Chloride Solution

Anodic polarization diagrams in deaerated and aerated 3.15wt% sodium chloride solution for BR-5, CP11-5, and CP13-5 electrodes are compared in Figure 5-7 and Figure 5-8, respectively.

![Anodic polarization diagrams of BR-5, CP11-5, and CP13-5 electrodes in deaerated 3.15wt% sodium chloride solution](image)

The curves of the BR-5, CP11-5, and CP13-5 showed the onset of pitting corrosion at approximately -0.73 V vs SCE (Figure 5-7).
In the aerated 3.15wt% sodium chloride solution (Figure 5-8), the open-circuit potentials (-0.74V vs SCE) were approximately coincident with the pitting potentials, indicating that all electrodes were pitting in the open-circuit condition. In the aerated solution, dissolved oxygen can polarize the electrodes to potentials greater than or approximately equal to the pitting potentials. The current density of the CP11-5 and CP13-5 was less than that of the BR-5; however, there was wide deviation, indicating that the decrease of the current density by the coatings varied on each electrode.

The anodic polarization diagrams in 3.15wt% sodium chloride solution for BR-6, CP11-6, and CP13-6 electrodes are compared in Figure 5-9 and Figure 5-10.
Figure 5-9 Anodic polarization diagrams of BR-6, CP11-6, and CP13-6 electrodes in deaerated 3.15wt% sodium chloride solution

Similarly to BR-5, the curve of BR-6 showed the onset of pitting corrosion at approximate -0.84V vs SCE (Figure 5-9). Although the current densities of the CP11-6 and CP13-6 were less than that of BR-6, the onset of pitting corrosion on both CP11-6 and CP13-6 was found at the approximately same potential of -0.84V vs SCE.
The open-circuit potentials were approximately -0.74 V vs SCE, and slightly positive to that of the pitting potentials. In the aerated solution, the dissolved oxygen can polarize the electrodes to potentials greater than or approximately equal to the pitting potential. The current densities of CP11-6 and CP13-6 were less than that of BR-6; however, there was wide deviation, indicating that the magnitude of current density depended on the condition of the coatings.

The comparison of BR-5 and BR-6 during anodic polarization in 3.15 wt% sodium chloride solution is shown for deaerated (Figure 5-11) and aerated (Figure 5-12) solutions.
Figure 5-11 Comparison of anodic polarization diagrams of BR-5 and BR-6 in deaerated 3.15wt% sodium chloride solution.

Figure 5-12 Comparison of anodic polarization diagrams of BR-5 and BR-6 in aerated 3.15wt% sodium chloride solution.
Pitting corrosion occurred on BR-5 and BR-6 in 3.15wt% sodium chloride solutions. The current densities of BR-5 was a little less than those of BR-6, indicating that the anodic dissolution occurred a little more preferably on Al6061-T6 than on Al5052-H3.

5.3 CATHODIC POLARIZATION

5.3.1 0.5M Sodium Sulfate Solution

Cathodic polarization diagrams in 0.5M sodium sulfate solution for BR-5, CP11-5, and CP13-5 electrodes are compared in Figure 5-13 and Figure 5-14.

The slope of the curve of the CP13-5 was a little steeper than those of the curves of the BR-5 and CP11-5 (Figure 5-13). For potential less than -1.2V vs SCE, the current density of the CP13-5 was less than that of the CP11-5 by an order of magnitude;
moreover, the current density of the CP11-5 was less than that of BR-5 by an order of magnitude. Near the open-circuit potential, the current density of both CP11-5 and CP13-5 electrodes was about one order of magnitude less than that of the BR-5.

![Cathodic polarization diagrams of BR-5, CP11-5, and CP13-5 electrodes in aerated 0.5M sodium sulfate solution](image)

Figure 5-14 Cathodic polarization diagrams of BR-5, CP11-5, and CP13-5 electrodes in aerated 0.5M sodium sulfate solution

The all curves (Figure 5-14) showed oxygen reduction between the open-circuit potential and approximately -1.3VvsSCE and hydrogen evolution below -1.3VvsSCE. Similar to the deaerated case(Figure 5-13),below the potential of hydrogen evolution initiation, the current density of the CP13-5 was less than that of the CP11-5 by an order of magnitude; moreover, the current density of the CP11-5 was less than that of BR-5 by one order of magnitude. However, in the region of oxygen reduction of between the open-circuit potential and about -1.15VvsSCE, the CP11-5 showed less current density than the CP13-5.
Cathodic polarization diagrams in 0.5M sodium sulfate solution for BR-6, CP11-6, and CP13-6 electrodes are compared in Figure 5-15 and Figure 5-16.

![Cathodic polarization diagram](image_url)

Figure 5-15 Cathodic polarization diagrams of BR-6, CP11-6, and CP13-6 electrodes in deaerated 0.5M sodium sulfate solution

The slope of the curve of the CP13-6 was a little steeper than those of the curves of the BR-6 and CP11-6 (Figure 5-15). The current density of CP13-6 was less than that of the CP11-6 by an order of magnitude; moreover, the current density of the CP11-6 was less than that of the BR-6 by an order of magnitude.
Figure 5-16 Cathodic polarization diagrams of BR-6, CP11-6, and CP13-6 electrodes in aerated 0.5M sodium sulfate solution

The all curves (Figure 5-16) showed oxygen reduction between the open-circuit potential and approximately -1.4V vs SCE and hydrogen evolution below -1.4V vs SCE. Similar to the deaerated case (Figure 5-15), below the potential of hydrogen evolution initiation, the current density of the CP13-6 was less than that of the CP11-6 by an order of magnitude, moreover, the current density of the CP11-6 was less than that of BR-6 by an order of magnitude. In the region of oxygen reduction of between the open-circuit potential and -0.8V vs SCE, the CP11-6 showed less current density than the CP13-6.

The Figure 5-17 and Figure 5-18 show the comparison of BR-5 and BR-6 cathodic polarization diagrams in 0.5M sodium sulfate solution.
Figure 5-17 Comparison of cathodic polarization diagrams of BR-5 and BR-6 in deaerated 0.5M sodium sulfate solution

Figure 5-18 Comparison of cathodic polarization diagrams of BR-5 and BR-6 in aerated 0.5M sodium sulfate solution
In deaerated 0.5M sodium sulfide solution (Figure 5-17), the cathodic hydrogen-evolution polarization curves for both BR-5 and BR-6 were identical. On the other hand, in aerated 0.5M sodium sulfide solution (Figure 5-18), the current density of the BR-5 was less than that of the BR-6 in the region of oxygen reduction, indicating that Al5052-H3 has better corrosion resistance than Al60161-T6 in the open-circuit potential condition.

5.3.2 3.15wt% Sodium Chloride Solution

Cathodic polarization diagrams in deaerated and aerated 3.15wt% sodium chloride solution for BR-5, CP11-5, and CP13-5 electrodes are compared in Figure 5-19 and Figure 5-20, respectively.

The slope of the curve of the CP13-5 was steeper than those of the curves of the BR-5 and CP11-5 (Figure 5-19). Between the open-circuit potentials and -1.3V vs SCE, the
current density of the CP13-5 was less than that of the CP11-5 by an order of magnitude; moreover, the current density of the CP11-5 was less than that of the BR-5 by an order of magnitude. Below -1.3V vs SCE, the current density of the CP13-5 was less than that of the CP11-5 by two orders of magnitude.

All curves showed oxygen reduction between the open-circuit potential and approximately -1.3V vs SCE and hydrogen evolution below -1.3V vs SCE (Figure 5-20). Near the open-circuit potential, CP11-5 showed slightly less current density than CP13-5, but higher current density than CP13-5 for all lower potentials.

Cathodic polarization diagrams in deaerated and aerated 3.15wt% sodium chloride solution for BR-6, CP11-6, and CP13-6 electrodes are shown in Figure 5-21 and Figure 5-22, respectively.
Figure 5-21 Cathodic polarization diagrams of BR-6, CP11-6, and CP13-6 electrodes in deaerated 3.15wt% sodium chloride solution.

The slope of all curves was similar (Figure 5-21). The current density of the CP13-6 was less than that of the CP11-6 by more than an order of magnitude.
The all curves (Figure 5-22) showed oxygen reduction between the open-circuit potential and approximately -1.4V vs SCE, and hydrogen evolution below that region. Below the potential of hydrogen evolution initiation, the current density of CP13-6 was less than that of CP11-6 by an order of magnitude; moreover, the current density of CP11-6 was less than that of BR-6 by an order of magnitude.

The Figure 5-23 and Figure 5-24 show the comparison of BR-5 and BR-6 cathodic polarization diagrams in deaerated and aerated 3.15wt% sodium chloride solutions, respectively.
Figure 5-23 Comparison of cathodic polarization diagrams of BR-5 and BR-6 in deaerated 3.15wt% sodium chloride solution

Figure 5-24 Comparison of cathodic polarization diagrams of BR-5 and BR-6 in aerated 3.15wt% sodium chloride solution
In deaerated 3.15wt% sodium chloride solution (Figure 5-23), both BR-5 and BR-6 have similar hydrogen evolution behavior. On the other hand, in aerated 3.15wt% sodium chloride solution (Figure 5-24), the current density of BR-5 was less than that of BR-6 in the region of oxygen reduction. This implies that Al5052-H3 has better corrosion resistance than Al6016-T6 in an open-circuit potential condition, which is similar to the behavior in 0.5M sodium sulfate solution.

5.4 MORPHOLOGICAL CHANGE INVESTIGATION

5.4.1 Bare (BR) Electrodes

In 3.15wt% sodium chloride solution, pitting corrosion should occur on anodic-polarized electrodes. In order to confirm that the pitting corrosion occurred on the anodic-polarized electrodes, morphological changes of anodic-polarized BR-6 electrodes in 3.15wt% sodium chloride solution and 0.5M sodium sulfate solution were inspected using an optical microscope. These images are shown in Figure 5-25 and Figure 5-26. Both figures are shown in magnifications of ten times and fifty times.

As Figure 5-25 shows, there were many tiny pits on the entire surface and black corrosion product deposits around the pits for the anodic-polarized BR-6 electrode in 3.15wt% sodium chloride solution. Contrarily, corrosion products and tiny pits were not found on the anodic-polarized BR-6 electrode in 0.5M sodium sulfate solution. From the results of anodic polarization tests, it can be said that these morphological changes on BR-6 electrode in 3.15wt% sodium chloride solution are pitting corrosion.
Moreover, in order to investigate morphological changes by cathodic reaction, the surface of cathodic-polarized BR-6 electrodes in 3.15wt% sodium chloride solution and 0.5M sodium sulfate solution were investigated. These images are shown in Figure 5-27 and Figure 5-28.

From these images, it is found that morphological change such as tiny pits occurred on the cathodic-polarized BR-6 electrodes similar to the anodic polarized electrode in 3.15wt% sodium chloride solution. However, the pits on the cathodically polarized electrode appear to be more uniform in size and distribution compared to the anodically polarized electrode in the 3.15wt% sodium chloride solution, where the pits appear larger and clustered. Also, there is no difference in morphological change on the
cathodic-polarized BR-6 electrodes between 3.15wt% sodium chloride solution and 0.5M sodium sulfate solution.

Figure 5-27 Images of an cathodic-polarized BR-6 electrode in 3.15wt% sodium chloride solution

Figure 5-28 Images of an cathodic-polarized BR-6 electrode in 0.5M sodium sulfate solution

Generally speaking, corrosion does not occur during cathodic polarization. However, according to Van de Ven and Koelmans[28], “cathodic corrosion” occurs when the hydroxide ion concentration increases at the electrode surface due to the hydrogen evolution on aluminum substrates. Moreover, Moon and Pyun[29] investigated the corrosion behavior of pure aluminum during cathodic polarization in deaerated acidic, neutral and alkaline solutions by measuring the weight loss, volumetric hydrogen evolution rate, open-circuit potential and potentiostatic current transients. They concluded that cathodic polarization helped the dissolution of pure aluminum only in the
neutral solution and the cathodic corrosion of pure aluminum proceeded by chemical
dissolution of an oxide film at the oxide/electrolyte interface and simultaneous oxide film
formation at the aluminum/oxide interface. These two studies confirm that the corrosion
on the cathodic-polarized BR-6 electrodes observed by optical microscope was cathodic
corrosion.

5.4.2 HCLCoat11-coated (CP11) Electrodes

Similar to the BR-6 electrode, the morphological changes on the CP11-6 electrode
in 3.15wt% sodium chloride solution were investigated by optical microscopy. Figure
5-29 shows the images of morphological changes on an anodic polarized CP11-6
electrode. From these images, it was found that pitting corrosion occurred with deposition
of corrosion products that fractured and de-laminated the HCLCoat11 film. This
morphological change was visually similar to that of the anodic-polarized BR-6 electrode
in 3.15wt% sodium chloride solution. Figure 5-30 shows that cathodic corrosion occurred
on the cathodic-polarized CP11-6 electrode similarly to the cathodic-polarized BR-6
electrode.

Figure 5-29 Images of an anodic-polarized CP11-6 electrode in 3.15wt% sodium chloride
solution
5.4.3 **HCLCoat13-coated (CP13) Electrodes**

The morphological changes on the CP13-6 electrode were also investigated by optical microscopy. Dissimilar to the anodic-polarized BR-6 and CP11-6 electrodes, almost no pitting corrosion occurred as shown in Figure 5-31. Also, the fewer pits that did form were much smaller than those of the anodic-polarized CP11-6 electrodes. Cathodic corrosion also occurred on the cathodic-polarized CP13-6 electrode; however, the amount of the cathodic corrosion is less than that of the cathodic-polarized CP11-6 electrode.
Figure 5-32 Images of a cathodic-polarized CP13-6 electrode in 3.15 wt% sodium chloride solution
6 RESULT SOF IMMERSION TEST

6.1 ARTIFICIAL ASTM SEAWATER IMMERSION

6.1.1 Visual Results

Figure 6-1 and Figure 6-2 show the visual results of short term (141 days) immersion coupons; Figure 6-3 and Figure 6-4, also, show the visual results of long term (243 days) immersion coupons. The immersion was conducted in air-exposed ASTM seawater at 30°C. It was found that the organic coatings of ES and PS coupons were significantly degraded and that almost all organic coatings delaminated on both Al5052-H3 and Al6061-T6. On the other hand, the organic coatings of EC and PC coupons looked like pristine and no corrosion occur on EC and PC coupons after 243 days immersion.

With regard to the stand-alone siloxane ceramic/polymer coatings, the CP11-5 coupons had no corrosion damage after 141 days immersion; however, the substrate changed dark in color after 243 days immersion. The CP11-6 coupons, also, had no corrosion damage after 141 days immersion; however, the edges of coupons became black after 243 days immersion due to the HCLCoat11 film spallation. The CP13-5 coupons had black spots due to corrosion on the edge of the coupon after 141 days immersion and the extent of corrosion increased for the 243 days immersion. For the CP13-6 coupons, there were more the black spots than on the CP13-5 coupons. In addition, the HCLCoat13 film was crazed and delaminated to some degree after the immersion test, indicating the seawater degraded the HCLCoat13 film.

The surface of BR-5 coupons after 141 days immersion was partially covered with white powder-like corrosion products, and the surface of BR-5 after 243 days immersion
was entirely covered and changed dark in color; on the other hand, the surface of the BR-6 coupons was covered with a dark-gray corrosion product film.

![Image showing BR-5, CP11-5, CP13-5, ES-5, PS-5, EC-5, PC-5 coupons]

**Figure 6-1Al5052-H3 coupons after 141 days immersion in air-exposed ASTM seawater at 30°C.**

The top row: no scribe side; the bottom row: the upper section: 1” scribe side
Figure 6-2Al6061-T6 coupons after 141 days immersion in air-exposed ASTM seawater at 30°C.

The top row: no scribe side; the bottom row: the upper section: 1” scribe side

Figure 6-3Al5052-H3 coupons after 243 days immersion in air-exposed ASTM seawater at 30°C.

The top row: no scribe side; the bottom row: the upper section: 1” scribe side
6.1.2 Areal Mass Change Rate

The results of an areal mass change rate by weight measurement are shown from Figure 6-5 to Figure 6-8. The BR-5 coupon after 141 days immersion gained mass due to the deposition of corrosion products which looked like white powder; however, for the BR-5 coupon after 243 days immersion the dissolution of an aluminum alloy made the net mass change negative. The BR-6 coupons after both 141 days and 243 days immersion gained mass since the dissolution of an aluminum alloy was surpassed by the deposition of corrosion products.

The CP11-5 and CP11-6 coupons lost mass for both 141 days and 243 days immersion and the longer immersion resulted in more mass loss. The CP13-5 and CP13-6 coupons also lost mass for both 141 days and 243 days immersion. The CP13 coupons lost
mass more than the CP11 coupons, indicating that HCLCoat13 film may have degraded to a greater degree than the HCLCoat11 film.

With regard to the two-coat systems, the coupons with the HCLCoat13 undercoat (i.e., ES-5 and ES-6 coupons) lost the most mass among the 6 coating schemes and bare coupons. The epoxy film of almost all ES coupons delaminated and severe corrosion occurred beneath the epoxy film. On the other hand, the aerial mass change rate of the PS coupons depended on the coupon. Some PS coupons had negative aerial mass change rate due to the delamination of the polyurethane film, while other PS coupons had positive mass change due to the accumulation of corrosion products beneath the polyurethane film.

As the visual results showed, there was no corrosion damage on the two-coat coupons with the chromate conversion coating as the undercoat treatment. It is assumed that the negative aerial mass change rate indicated that the top organic coating either leached out volatile components or dissolved and became thinner.

![Figure 6-5 Areal mass change rate of Al5052-H3 coupons for 141 days immersion](image)

Figure 6-5 Areal mass change rate of Al5052-H3 coupons for 141 days immersion
Figure 6-6 Areal mass change rate of Al6061-T6 coupons for 141 days immersion

Figure 6-7 Areal mass change rate of Al5052-H3 coupons for 243 days immersion
6.1.3 Morphological Change Investigation

The surface of BR, CP11, and CP13 coupons observed with optical microscopy is shown between Figure 6-9 and Figure 6-14. There was some pitting corrosion on the BR coupons and semitransparent scales partly covered the coupon surface. For the CP11 and CP13 coupons, they had different morphological changes. The CP11 coupons had many tiny round pits on the surface, while the CP13 coupons had patches of corrosion damage where the HCLCoat13 film crazed and partly broke away.
Figure 6-10 BR coupons after 243 days immersion

Figure 6-11 CP11 coupons after 141 days immersion

Figure 6-12 CP11 coupons after 243 days immersion

Figure 6-13 CP13 coupons after 141 days immersion
6.2 INTERTIDAL IMMERSION

6.2.1 Visual Results

Figure 6-15 and Figure 6-16 show the visual results of short term (132 days) immersion coupons; Figure 6-17 and Figure 6-18, also, show the visual results of long term (224 days) immersion coupons. The coupons were exposed in the splash-spray zone at Coconut Island, Oahu. There were marine organisms such as algae and sponges on the surface of all coupons. It was hypothesized that the marine organisms may have impeded corrosion on the coupons.

The epoxy film of the ES coupons in the artificial ASTM seawater immersion tests delaminated and severe corrosion occurred beneath the epoxy film; contrarily, in the splash-spray zone, severe corrosion did not appear to occur beneath the epoxy film, although some coating delamination was observed. The polyurethane film of PS coupons also did not delaminate. There was no corrosion damage on the EC and PC coupons.

With regard to the stand-alone siloxane ceramic/polymer coatings, the CP11-5 coupons had no corrosion damage after 132 days immersion; the CP11-6 coupons, also, had no corrosion damage after 132 days immersion; however, there were corrosion products on the edge of the CP11-5 coupons after 224 days immersion due to film

Figure 6-14 CP13 coupons after 243 day immersion
spallation. The CP13-5 coupons had corrosion products on the edge of the coupon after 132 days immersion and the amount of corrosion increased for coupons after 224 days immersion. For the CP13-6 coupons, there were more corrosion spots than on the CP13-5 coupons. In addition, the HCLCoat13 film was crazed and delaminated.

The surface of BR-5 coupons after 132 days immersion had almost no corrosion damage; however, corrosion sporadically occurred on the surface of BR-5 after 224 days immersion. For the BR-6 coupons, corrosion sporadically occurred on the surface both after 132 days and 224 days immersion.

In addition to corrosion damage, there were brown spots on the surface (e.g., CP13-5, PC-5, PC-6, and PC-6) after 224 days immersion. The brown spots were caused by marine organisms and the initial coupon cleaning could not remove them.

![Image of coupons](image_url)

Figure 6-15 Al5052-H3 coupons after 132 days exposure to the splash-spray zone at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side


Figure 6-16 Al6061-T6 coupons after 132 days exposure to the splash-spray zone at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side

Figure 6-17 Al5052-H3 coupons after 224 days exposure to the splash-spray zone at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side
Figure 6-18 Al6061-T6 coupons after 224 days exposure to the splash-spray zone at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side

6.2.2 Areal Mass Change Rate

The results of an areal mass change rate by weight measurement are shown in Figure 6-19 through Figure 6-22. The BR-5 and BR-6 coupons did not lose significant mass as the biofilm of algae may have attenuated severe corrosion damage.

The CP11-5 and CP11-6 coupons increasingly lost mass with the exposure periods of 132 days and 224 days. The CP13-5 and CP13-6 coupons also lost mass for both 132 days and 224 days immersion, although one of CP11-5 coupons gained mass after 224 days immersion. The CP13 coupons lost mass more than the CP11 coupons, indicating that HCLCoat13 film might degrade and delaminate more than the HCLCoat11 film.
With regard to the two-coat systems with the HCLCoat13 under-coat treatment, the ES-5 and ES-6 coupons lost the most mass among the 6 coating schemes and bare coupons which was similar to artificial ASTM seawater tests. The epoxy film of almost all ES coupons delaminated; however, severe corrosion did not occur beneath the epoxy film which was contrary to the ES coupons exposed in the artificial ASTM seawater. Also, the aerial mass change rate of almost all PS coupons lost mass, indicating that the polyurethane film thinned or delaminated.

As the visual results showed, there was no corrosion damage on the two-coat coupons with the chromate conversion under-coat treatment. Similarly to the artificial ASTM seawater immersion tests, it was assumed that the negative aerial mass change rate was due to leaching of volatile components in the organic top coat or thinning of the coating.

![Figure 6-19 Areal mass change rate of Al5052-H3 coupons for 132 days exposure to the splashespray zone at Coconut Island, Oahu](image)
Figure 6-20 Areal mass change rate of Al6061-T6 coupons for 132 days exposure to the splash-spray zone at Coconut Island, Oahu

Figure 6-21 Areal mass change rate of Al5052-H3 coupons for 224 days exposure to the splash-spray zone at Coconut Island, Oahu
6.2.3 Morphological Change Investigation

The surface of BR, CP11, and CP13 coupons observed with optical microscopy is shown in Figure 6-23 through Figure 6-28. There was some pitting corrosion on the BR-5 coupons and the BR-6 coupons. The corrosion damages could not been found on the CP11 coupons. The CP13 coupons also did not have obvious corrosion damage; however, the HCLCoat13 film partially delaminated.
Figure 6-24 BR coupons after 224 days exposure to the splash-spray zone at Coconut Island, Oahu.

Figure 6-25 CP11 coupons after 132 days exposure to the splash-spray zone at Coconut Island, Oahu.

Figure 6-26 CP11 coupons after 224 days exposure to the splash-spray zone at Coconut Island, Oahu.
6.3 WARM SURFACE SEAWATER IMMERSION

6.3.1 Visual Results

Figure 6-30 and Figure 6-31 show the visual results of short term (142 days) immersion coupons, Figure 6-32 and Figure 6-33, also, show the visual results of long term (204 days) immersion coupons. Algae, sponge, oysters, and barnacles thrived on the surface of coupons. It is assumed that the marine organisms impeded corrosion on the coupons.

The epoxy coating of the ES coupons and polyurethane film of the PS coupons did not delaminate because the biological growth on the coupons such as algae and...
sponges provided some protection. On the other hand, the macrofouling caused severe corrosion to occur on the bare coupons; especially, BR-6 coupons.

With regard to the stand-alone siloxane ceramic/polymer coatings, the CP11-5 coupons had no corrosion damage after 142 days immersion and the CP11-6 coupons showed corrosion only on the edge of the coupons due to the spallation of the coating. For the CP13 coupons, the HCLCoat13 film was degraded by the seawater.

The EC and PC coupons did not show corrosion damage; however, the organic coatings appeared to have thinned.

The initial coupon cleaning was insufficient to remove marine organisms from the coupons (Figure 6-29), except for the CP11 coupons from which the biofouling was easily remove. This indicates that the HCLCoat11 also has good anti-fouling characteristics.

Figure 6-29 Marine organisms on coupons between a coupon rack and coupons
Figure 6-30Al5052-H3 coupons after 142 days immersion in warm surface seawater at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side

Figure 6-31Al6061-T6 coupons after 142 days immersion in warm surface seawater at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side
Figure 6-32Al5052-H3 coupons after 204 days immersion in warm surface seawater at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side.

Figure 6-33Al6061-T6 coupons after 204 days immersion in warm surface seawater at Coconut Island, Oahu. The top row: no scribe side; the bottom row: the upper section: 1” scribe side.
6.3.2 Areal Mass Change Rate

The results of an areal mass change rate by weight measurement are shown in Figure 6-34 through Figure 6-37. Since marine organisms thrived on the surface, and the initial coupon cleaning could not remove all of the marine organisms, the areal mass change rates of almost half coupons were positive. The aerial mass change rate primarily indicates biofouling. As mentioned in the visual results section, the initial coupon cleaning for the coupons coated with HCLCoat11 easily removed almost all marine organisms. The aerial mass change rates (Figure 6-34) of the CP11 coupons were smaller than other coupons, indicating the ease with which the HCLCoat11 film allowed macrofouling to be removed from the surface. The coupons which the organic epoxy or polyurethane top coatings had significantly more biofouling.

Figure 6-34 Areal mass change rate of Al5052-H3 coupons for 142 days immersion in warm surface seawater at Coconut Island, Oahu.
Figure 6-35 Areal mass change rate of Al6061-T6 coupons for 142 days immersion in warm surface seawater at Coconut Island, Oahu.

Figure 6-36 Areal mass change rate of Al5052-H3 coupons for 204 days immersion in warm surface seawater at Coconut Island, Oahu.
Figure 6-37 Areal mass change rate of Al6061-T6 coupons for 204days immersion in warm surface seawater at Coconut Island, Oahu.

### 6.3.3 Morphological Change Investigation

The surface of BR, CP11, and CP13 coupons observed with optical microscopy is shown in Figure 6-38 through Figure 6-43. The BR-5 and BR-6 coupons had pitting corrosion and semitransparent scales almost entirely covered the surface of the coupons. The BR-6 coupons had more corrosion damages than the BR-5 coupons. Similar to the CP11 coupons in the artificial ASTM seawater immersion test, the CP11 coupons had many tiny round corrosion pits. On the other hand, significant corrosion damage could not be found on CP13 coupons; however, HCLCoat13 film showed some degradation and partly broke away.
Figure 6-38 BR coupons after 142 days immersion in warm surface seawater at Coconut Island, Oahu.

Figure 6-39 BR coupons after 204 days immersion in warm surface seawater at Coconut Island, Oahu.

Figure 6-40 CP11 coupons after 142 days immersion in warm surface seawater at Coconut Island, Oahu.
Figure 6-41 CP11 coupons after 204 days immersion in warm surface seawater at Coconut Island, Oahu.

Figure 6-42 CP13 coupons after 142 days immersion in warm surface seawater at Coconut Island, Oahu.

Figure 6-43 CP13 coupons after 204 days immersion in warm surface seawater at Coconut Island, Oahu.

6.4 COLD DEEP SEA WATER IMMERSION

6.4.1 Visual Results

Figure 6-44 and Figure 6-45 show the visual results of short-term (39 days) immersion coupons exposed to cold deep seawater at Kona, Hawaii. All of the coupons
excluding the BR coupons and ES coupons looked almost pristine. Both BR-5 and BR-6 coupons became dark; the BR-6 coupon looked darker than the BR-5 coupon.

For the ES coupons, there were some white corrosion products beneath the epoxy film; however, the epoxy film did not grossly delaminate.

The visual results of CP13 coupons show that the HCLCoat13 film was not degraded by the seawater immersion. On the other hand, the visual results of the CP11 coupons show that there was some spallation on the edge of the coupons.

Figure 6-44Al5052-H3 coupons after 39 days immersion in cold deep seawater at Kona, Hawaii.

The top row: no scribe side; the bottom row: the upper section: 1” scribe side
6.4.2 Areal Mass Change Rate

The results of an areal mass change rate by weight measurement are shown in Figure 6-46 and Figure 6-47. The areal mass change rates of this immersion test have different characteristics from those of the other immersion tests. First, the aerial mass change rates of CP11 coupons were greater than those of CP13 coupons. Second, the aerial mass change rates of EC coupons were positive although there was no corrosion product on the surface. Third, the ES-5 coupons gain mass while the ES-6 coupons lost mass.
Figure 6-46 Areal mass change rate of Al5052-H3 coupons for 39 days immersion in cold deep seawater at Kona, Hawaii

Figure 6-47 Areal mass change rate of Al6061-T6 coupons for 39 days immersion in cold deep seawater at Kona, Hawaii
6.4.3 Morphological Change Investigation

The surface of BR, CP11, and CP13 coupons observed with optical microscopy is shown in Figure 6-48 through Figure 6-50. Dissimilar to other immersion tests, there was no pitting corrosion on the BR coupons. A semitransparent scale deposited on the BR-6 coupons. Also, CP11 and CP13 coupons did not have obvious corrosion damages. Both siloxane ceramic/polymer films were not been degraded.

Figure 6-48 BR coupons after 39 days immersion in cold deep seawater at Kona, Hawaii

Figure 6-49 CP11 coupons after 39 days immersion in cold deep seawater at Kona, Hawaii

Figure 6-50 CP13 coupons after 39 days immersion in cold deep seawater at Kona, Hawaii
6.5 COMPARISON OF CORROSION RATE (BARE COUPONS) AMONG IMMERSION TESTS

After the initial coupon cleaning, the BR coupons were cleaned by phosphoric acid solution with chromium trioxide in order to remove corrosion products deposited on the surface. The weight loss after the cleaning with the phosphoric acid solution can be used to determine actual corrosion rates. The corrosion rates of BR coupons after phosphoric acid solution cleaning are shown in Figure 6-51.

From the Figure 6-51, BR coupons were significantly corroded in warm surface seawater immersion. Moreover, judging from the visual results, macrofouling accelerated corrosion damages, especially on BR-6 coupons, in the warm surface seawater immersion. For other immersion tests, it is found that the corrosion rates were almost same values.

![Figure 6-51 Corrosion rates of BR coupons of all immersion tests](image)

6.6 COMPARISON OF DAMAGE AREA FRACTION AMONG IMMERSION TESTS

Area fractions of damaged coating area were determined using MATLAB from the x100 magnification optical microscopy image in the sections of 6.1.3, 6.2.3, 6.3.3,
and 6.4.3. The result of the damage area fraction is shown in Figure 6-52. From this result, it is found that there was no significant difference among immersion tests. Comparing the damage area fraction between Al5052-H3 and Al6061-T6, generally speaking, Al5052-H3 coupons had less damage than Al6061-T6 coupons. Moreover, CP11-6 coupons had more damage than other the siloxane ceramic/polymer coupons. As the optical microscopy image showed, the CP11-6 coupons had more tiny round corrosion pits than the CP11-5 coupons, resulting in the CP11-6 having a larger damage area fraction.

The damage area fractions of ES, PS, EC, and PC were not included in this figure because the organic coatings of the ES and PS coupons apparently delaminated; on the other hand, there was no corrosion damage on the EC and PC coupons.

![Figure 6-52 Damage area fractions BR, CP11, CP13 coupons in all immersion tests](image)

Figure 6-52 Damage area fractions BR, CP11, CP13 coupons in all immersion tests


7 DISCUSSION

7.1 CORROSION BEHAVIOURBENEATH CERAMIC/POLYMER FILMS

Observing morphological changes in the polarization test electrodes allows one to elucidate the corrosion features caused by both the anodic and cathodic reactions. Moreover, comparing morphological changes on immersion coupons with those on the electrodes should help to elucidate corrosion initiation processes during immersion.

7.1.1 Pitting Corrosion beneath the Films during Anodic Polarization

Pitting corrosion occurs when chloride ions reaches the aluminum substrate and prevents the formation of a continuous passive oxide layer. There are three plausible explanations for why pitting corrosion occurred on the coated electrodes in 3.15wt% sodium chloride solution. First, the film broke down due to the applied potential of the polarization scan that imparts an electric field through the coating that is higher than the dielectric strength. Second, the anodic current emanates from the preexisting breaches in the film where bare aluminum is exposed. Third, chloride ions have the ability to penetration into the siloxane ceramic/polymer coatings due to the small size and high mobility.

The first postulate that the coating breaks down due to the applied potential of the polarization scan will be discussed. If the coating breaks down due to the applied potential, the coating should also break down for anodic polarization in 0.5M sodium sulfate solution. The surfaces of anodic-polarized CP11-6 and CP13-6 electrodes are shown in Figure 7-1andFigure 7-2. Since cracks or holes cannot be found in Figure 7-2, the HCLCoat13 film likely did not break down due to the applied potential of the polarization scan. With regards to the HCLCoat11 coating, a gray deposit is found
between the HCLCoat11 film and a substrate; however, apparent cracks are not found for anodic polarization in 0.5M sodium sulfate solution (Figure 7-1). According to Hihara[30], coating breaches did not nucleate during anodic polarization for some plasma-enhanced chemical vapor deposited ceramic coating. It were estimated that the electric field through the coating would be on the order of only 1MV/m, assuming a potential drop of 1V through the film of 1µm thickness. The dielectric strength of insulating films can be as high as 1000MV/m.

Considering the result of no apparent cracks in the HCLCoat11-coated electrodes and Hihara’s study, it can be concluded that the HCLCoat11 film also does not break down due to the applied potential of the polarized scan. Therefore, the first postulate can be denied.

Figure 7-1 Optical microscope images of an anodic-polarized CP11-6 electrode in 0.5M sodium sulfate solution
The second postulate that the anodic current emanates from preexisting breaches on coatings will be discussed. In order to confirm that there are preexisting breaches on the coatings, surfaces of pristine coating coupons were investigated with optical microscopy. The images are shown in Figure 7-3 and Figure 7-4. From these images, it was found that the HCLCoat11 film had many small pores.
Further investigation for the pristine coating samples were conducted with the SEM. The images are shown in Figure 7-5 and Figure 7-6. The SEM images show that the HCLCoat11 film had many small pores with diameters between 1 and 2µm, and the HCLCoat13 film had fewer pores whose diameter generally smaller than 1µm. Based on these findings, it is likely that the anodic current emanated from the preexisting breaches, resulting in corrosion initiation from these pores.
The third postulate that chloride ions have the ability to penetration into the siloxane ceramic/polymer coatings due to the small size and high mobility of a chloride ion will be discussed. The penetration through the coating films is classified into two mass transfer modes: diffusion and migration.

Diffusion is movement of species under the influence of a chemical potential gradient such as a concentration gradient. It is possible for chloride ions to penetrate the coatings and reach the substrate. Thus, the time in which the chloride ion can reach the substrate through the siloxane ceramic/polymer coating will be estimated. The time is determined as follows:

Assuming that a flux due to the diffusion is \( J \) (mol/s/cm²),

\[
Jt = D \frac{C_0}{\Delta} t
\]

Where \( t \) is the time, \( \Delta \) is the distance which the chloride ion diffuses, and \( D \) is the diffusion coefficient. From Figure 7-7,

\[
D \frac{C_0}{\Delta} t = \frac{C_0}{2} \Delta
\]

Solving the equation with \( t \),
In order to estimate the time for the chloride ion to diffuse through the coating, the chloride ion diffusion coefficient is required. However, since the chloride ion diffusion coefficient for the HCLCoat11 and HCLCoat13 coating is unknown, a chlorine diffusion coefficient in silica glass (SiO$_2$) at room temperature will be used. According to the study on the chlorine diffusion coefficient in SiO$_2$, the chlorine diffusion coefficient, D, between 1000-2000°C can be described by an Arrhenius equation: \[ \log_{10} (D \text{ [cm}^2\text{/s]}) = -3.55 - \frac{11000K}{T} \] [31, 32]. Although the room temperature is out of range for the equation, it is assumed that extrapolating down to the room temperature allows us to determine the chlorine diffusion coefficient at 25.5°C. Substituting 298.5K into the equation, the chlorine diffusion coefficient can be estimated as $4.0 \times 10^{-41} \text{cm}^2\text{/s}$. Assuming that the diffusion coefficient is $4.0 \times 10^{-41} \text{cm}^2\text{/s}$ and the film thickness is 1µm[12], the time for diffusion through the coating is $8.1 \times 10^{31}$ seconds, which is $146 \times 10^{22}$ days. Therefore, based on this estimated D, it is impossible for the chloride ion to reach an aluminum substrate due to the diffusion during the anodic polarization test since the anodic polarization test takes only about 30 minutes.

Migration is movement of charged species under influence of an electric field, which is the electrical potential gradient. The time of migration is derived as follows: The flux due to the migration of J (mol/s/cm$^2$) is determined by

\[ J = \frac{zFDC}{RT} \nabla \phi \]
where $z$ and $C$ are the charge and concentration of the specie, $D$ is the diffusion coefficient, $F$ is Faraday’s constant, $T$ is temperature, and $\nabla \phi$ is the potential gradient.

Similarly to the diffusion case,

$$\frac{zFC_0}{RT} \nabla \phi t = \frac{C_0}{2} \Delta$$

Solving the equation with $t$,

$$t = \frac{\Delta RT}{2zFD\nabla \phi}$$

Assuming that the chloride ion migrates in the potential gradient of $1.0 \times 10^6 \text{V/m}$ (the thickness of the coating is $1 \mu \text{m}[12]$ and the potential is $1 \text{V}$), the time is $3.2 \times 10^{28}$ seconds which is $374 \times 10^{21}$ days. It is also impossible for the chloride ion to reach the substrate due to the migration during anodic polarization test.

Figure 7-7 Linear concentration profile for steady-state diffusion across a coating

From this discussion, it can be concluded that the anodic current emanates from the preexisting breaches. The HCLCoat11film has more breaches than the
HCLCoat13 film, indicating that the HCLCoat13 film prevent anodic current from emanating through the film. This finding coincides with the results that the anodic current densities of the CP13-6 electrodes were less than those of the CP11-6 electrodes in Figure 5-7, Figure 5-8, Figure 5-9, and Figure 5-10.

7.1.2 Cathodic Corrosion beneath the Film during Cathodic Polarization

From the optical microscopy investigation of the morphological changes on cathodic-polarized electrodes, it was found that cathodic corrosion occurred on BR-6, CP11-6 and CP13-6 electrodes. Moreover, the CP11-6 electrode was found to have more cathodic corrosion than the CP13-6. Similar to the case of anodic pitting due to anodic polarization, the size and number of pre-existing breaches on the films were proportional to the amount of the cathodic corrosion. Therefore, it can be concluded that cathodic corrosion also occurred through the preexisting breaches.

7.1.3 Corrosion Behavior on Immersion Test Coupons

In order to understand corrosion behavior at the open-circuit potential condition, morphological changes were investigated with optical microscopy for the artificial ASTM seawater immersion test coupons in the section 6.1.3. According to the optical micrographs in the section, different morphological changes occurred on BR, CP11, and CP13 coupons.

The corrosion behavior on BR coupons will be discussed. It was found that pitting corrosion occurred and semitransparent calcareous scale covered the BR coupons. In order to observe the pitting sites, pitting corrosion sites were further investigated with the SEM. These images are shown in Figure 7-8. It was found that pitting corrosion occurred
around precipitates from Figure 7-8. The precipitates likely induced a galvanic cell with the aluminum matrix. The aluminum matrix is the anodic site and therefore dissolves.

![SEM images](image_url)

**Figure 7-8 SEM images of pitting corrosion sites on BR coupons**

With regarding to the CP11 coupons, it was found that localized corrosion damage occurred beneath the HCLCoat11 film. This morphological change was similar to that of cathodic-polarized CP11 electrodes. Therefore, it can be assumed that the corrosion damage on the CP11 coupons was cathodic corrosion. The reason why cathodic corrosion predominately occurs over anodic pitting corrosion will be discussed.

Chloride ions first reach substrate through coating breaches and prevent passivation. The exposed aluminum substrate forms a micro galvanic cell; at the anodic site, aluminum dissolves: \( \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \), and at the cathodic site, oxygen reduction occurs: \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \). In the case of the CP11 coupons, the hydroxide ions generated by the cathodic reaction do not readily diffuse into the bulk solution and concentrate at the substrate in the breaches. Consequently, the hydroxide ions generated by the cathodic reaction dissolve the oxide layer: \( \text{Al}_2\text{O}_3 + 2\text{OH}^- \rightarrow \text{AlO}_2^- + \text{H}_2\text{O} \), and the exposed aluminum reacts with water: \( 2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \) [29], the electrons generated by the aluminum dissolution are consumed for oxide reduction(Figure 7-9).
These reactions at a cathodic site promote each other; therefore, it is assumed that the cathodic corrosion predominantly occurs over anodic pitting corrosion in this case.

For CP13 coupons, it was observed that some corrosion damage occurred and the HCLCoat13 film crazed and partially delaminated. The further observation was conducted by SEM in order to investigate the corrosion initiation. The SEM images are shown in Figure 7-10. The left image of Figure 7-10 shows crazed and broken film. Pitting corrosion similar to the corrosion on BR coupons was observed in the right image of Figure 7-10. From this investigation, it is concluded that the seawater degraded the HCLCoat13 film before cathodic or pitting corrosion occurred.
Figure 7-10 SEM images of corrosion sites on HCLCoat13-coated coupons

For the immersion tests, there was slightly difference between the type of damage observed in the artificial ASTM seawater and natural seawater. First, the CP11 and CP13 coupons of the cold deep seawater immersion test did not show corrosion damage; however, this may have been caused by the short exposure period (39 days). The CP11 coupons from the other immersion tests (artificial ASTM seawater, intertidal, warm surface seawater) showed cathodic corrosion, and the HCLCoat13 film crazed and broke away from the CP13 coupons. Second, the BR coupons of the cold deep seawater immersion corroded differently from the BR coupons of other immersion tests. Pitting corrosion was found on the BR coupons of the artificial ASTM seawater, intertidal, warm surface seawater immersion tests; however, the BR coupons of the cold deep seawater immersion test did not have obvious pitting corrosion. The corrosion on the cold deep seawater coupons showed the surface of the BR coupons became dark. According to a report[4] on corrosion of candidate materials of use in an OTEC plant, one difference between cold seawater and warm seawater is the amount of magnesium ions. The cold seawater has less magnesium ions. The lower content of magnesium ions could suppress the formation of Mg(OH)$_2$ on cathodic sites, thereby increasing corrosion rates.
Unfortunately, due to the short exposure period (39 days), a direct comparison with the other conditions could not be made.

7.2 EVALUATION AS CORROSION RESISTANCE MATERIALS

7.2.1 Corrosion Current Density from Polarization Test

As the first step of corrosion evaluation, a corrosion current density will be determined from the results of the aerated cathodic polarization test. An extrapolation method can provide the corrosion current density. As Figure 7-11 shows, the cathodic polarization curve of potential versus logarithm of current density is non-linear at low over-potentials but becomes linear at higher over-potentials. The crossed point between the extrapolation of the linear region and open-circuit potential gives the corrosion current density, \( i_{\text{corr}} \) at \( E_{\text{corr}} \).

In order to determine the corrosion current densities of six type aluminum alloy coupons; BR-5, BR-6, CP11-5, CP11-6, CP13-5, and CP13-6, the cathodic polarization curves in Figure 5-20 and Figure 5-22 are used. The linear regions in the curves with logarithm of current density are assumed as shown in Table 7-1.
Table 7-1 Linear regions of cathodic polarization curves

<table>
<thead>
<tr>
<th>Linear Regions</th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>-6~5.75</td>
<td></td>
<td></td>
<td></td>
<td>-6~4.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-6.5~5.5</td>
<td>-6.5~5.5</td>
<td>-6.5~5.5</td>
<td>-6~5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Defining that “x” is the logarithm of current density and “y” is the potential, the Least Square Method provides regression lines from the linear regions;

BR-5: \( y = -0.431x - 3.407 \)

BR-6: \( y = -1.649x - 9.001 \)

CP11-5: \( y = -0.393x - 3.475 \)

CP11-6: \( y = -0.583x - 4.257 \)

CP13-5: \( y = -0.373x - 3.437 \)

CP13-6: \( y = -1.111x - 7.590 \)

The open-circuit potentials are also determined from Figure 5-20 and Figure 5-22.

The open-circuit potentials are shown in Table 7-2.

Table 7-2 Open-circuit potentials of cathodic polarization curves

<table>
<thead>
<tr>
<th>OCP [V vs SCE]</th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.765</td>
<td></td>
<td>-0.845</td>
<td>-0.813</td>
<td>-0.741</td>
<td>-0.746</td>
<td>-0.735</td>
</tr>
</tbody>
</table>

Substituting these open-circuit potentials into \( y \) of the regression line equations, \( x \) of logarithm of current density is determined as follows:

BR-5: \( x = (-0.765 + 3.407)/-0.431 = -6.137 \)

BR-6: \( x = (-0.741 + 9.001)/-1.649 = -5.010 \)

CP11-5: \( x = (-0.845 + 3.475)/-0.393 = -6.686 \)

CP11-6: \( x = (-0.746 + 4.257)/-0.583 = -6.023 \)
From these calculations, corrosion current densities are determined as shown in Table 7-3.

<table>
<thead>
<tr>
<th></th>
<th>BR-5</th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>BR-6</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{corr}$ [A/cm²]</td>
<td>7.287×10⁻⁷</td>
<td>2.060×10⁻⁷</td>
<td>9.039×10⁻⁸</td>
<td>9.775×10⁻⁹</td>
<td>9.474×10⁻⁷</td>
<td>6.733×10⁻⁷</td>
</tr>
</tbody>
</table>

### 7.2.2 Influence of Microstructure on Corrosion Current Density

The difference of the corrosion current densities between two alloys will be discussed in the viewpoint of their microstructure. The corrosion current densities determined from the polarization tests shows that the Al5052-H3 has better corrosion resistance than Al6061-T6 at open-circuit condition. The corrosion resistance of alloys depends on their microstructure as explained in 1.1.1. The Al5052-H3 is a strain hardening alloy and magnesium is largely present in solid solution in wrought alloys. It appears as eutectic Mg₂Al₃ in increasing amounts in as-cast ingots as the magnesium content increases. The Al6061-T6 is age hardening alloy and is formulated to make use of the solubility of Mg₂Si. If there is no manganese or chromium present, the iron-rich phases are Fe₃SiAl₁₂, Fe₂Si₂Al₉, or a mixture of the two, depending on the proportions of magnesium, silicon, and iron.

Figure 7-12 shows optical microscopy images of Al5052-H3 and Al6061-T6 metallographic samples. It is found that there are several second phase particles in the area surrounded by blue line in the Al6061-T6 image; on the other hand, the particles
in Al5052-H3 are less and smaller than those of Al6061-T6. This indicates that Al6061-T6 should have more local corrosion cells resulting from these precipitates, and it should promote pitting attack of the surface in an electrolyte; consequently, the corrosion rate of Al6061-T6 is greater than that of Al5052-H3.

![Precipitates of Al5052-H3 and Al6061-T6](image)

**Figure 7-12 Precipitates of Al5052-H3 and Al6061-T6**

### 7.2.3 Corrosion Rates and Inhibitory Power

The corrosion current density determined by the extrapolation method can provide a corrosion rate. The corrosion rate (mdd: milligrams per square decimeter per day) is converted from the corrosion current density as follows:

\[
\frac{mg}{dm^2 \cdot day} = i_{corr} \left( \frac{C}{cm^2} \right) \times \frac{24 \times 60 \times 60}{1} \left[ \frac{s}{day} \right] \times \frac{100}{1} \left[ \frac{cm^2}{dm^2} \right] \times \frac{1}{3 \times 96500} \left[ \frac{mol}{C} \right] \times 27 \left[ \frac{g}{mol} \right] \times 10^3 \left[ \frac{mg}{g} \right].
\]

Substituting the current densities determined by the extrapolation method into the above equation, the corrosion rates are determined as follows:

- **BR-5:** \( mdd = 0.728 \times 10^{-6} \times 8.058 \times 10^5 = 0.578 \)
- **BR-6:** \( mdd = 9.775 \times 10^{-6} \times 8.058 \times 10^5 = 7.877 \)
- **CP11-5:** \( mdd = 2.060 \times 10^{-7} \times 8.058 \times 10^5 = 0.166 \)
- **CP11-6:** \( mdd = 9.474 \times 10^{-7} \times 8.058 \times 10^5 = 0.763 \)
- **CP13-5:** \( mdd = 9.039 \times 10^{-8} \times 8.058 \times 10^5 = 0.073 \)
Also, average corrosion rates determined by the immersion tests (Figure 6-51) are shown in Table 7-4. With regarding to Al5052-H3, the corrosion rate determined by the extrapolation method is greater than the corrosion rates from the immersion tests other than those of the warm surface seawater immersion test. On the other hand, the corrosion rate of Al6061-T6 determined by the extrapolation method is greater than those of Al6061-T6 from all immersion tests. As mentioned in the section 6.5, macrofouling may have accelerated corrosion damage in the warm surface seawater immersion. Thus, the corrosion rates from the immersion tests except those from the warm surface seawater immersion are smaller than the corrosion rates determined by the extrapolation method. This could be due to a corrosion product film which prevented corrosion from accelerating in the seawater. Accumulation of OH⁻ ions close to the aluminum surface leads to the precipitation of insoluble magnesium hydroxide and calcium carbonate such as a calcareous scale. They precipitate as a very thin film that slows down corrosion[1]. On the other hand, the extrapolation method used the measurement data of the cathodic polarization tests in which metal dissolution does not occur; thus, the corrosion rate is determined in the condition that aluminum alloys surface always expose to solution.

<table>
<thead>
<tr>
<th></th>
<th>TS#1-1</th>
<th>TS#1-2</th>
<th>TS#2-1</th>
<th>TS#2-2</th>
<th>TS#3-1</th>
<th>TS#3-2</th>
<th>TS#4-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR-5</td>
<td>0.390</td>
<td>0.304</td>
<td>0.430</td>
<td>0.345</td>
<td>1.045</td>
<td>0.901</td>
<td>0.238</td>
</tr>
<tr>
<td>BR-6</td>
<td>0.305</td>
<td>0.263</td>
<td>0.330</td>
<td>0.848</td>
<td>2.486</td>
<td>4.730</td>
<td>0.532</td>
</tr>
</tbody>
</table>

Moreover, the corrosion rates for Al6061-T6 were lower than those of Al5052-H3 in the artificial ASTM seawater and the 132days intertidal exposure. Except for the
artificial ASTM seawater immersion and the 132days intertidal exposure, the trend in corrosion rates of Al5052-H3 and Al6061-T6 coincide with the results of the polarization tests, and the discussion about the influence of microstructure on corrosion in 7.2.2. This is considered to be due to the precipitation of insoluble magnesium hydroxide and calcium carbonate (semitransparent calcareous scales). EDXA showed that magnesium and calcium were present in the film. The electrolyte was stagnant in the artificial ASTM seawater immersion test, while natural seawater in other immersion tests flowed around coupons. The stagnation of electrolyte is considered to form the semitransparent calcareous scales; consequently, this made the corrosion rates in artificial ASTM seawater immersion lower than those in other immersion tests. The cathodic current density of a BR-6 electrode was greater than that of a BR-5 electrode (Figure 5-24), indicating that the semitransparent calcareous scale covered more on BR-6 coupons than on BR-5 coupons during the seawater immersion tests. Although corrosion rates of the siloxane ceramic/polymer coated coupons was not determined since the conventional cleaning using the phosphoric acid solution with chromium trioxide cannot remove the films, the calculated corrosion rates of the CP11 and the CP13 coupon showed that both ceramic/polymer films served as a corrosion barrier film and the HCLCoat13 film could prevent corrosion from occurring more than the HCLCoat11 film.

In order to evaluate the corrosion mitigation by the films, the inhibitory power $I\%$ is calculated from the following equation [33]: 

$$I\% = \frac{i_{corr(BR)} - i_{corr(CP11, CP13)}}{i_{corr(BR)}} \times 100.$$ 

The inhibitory powers of the films are shown in Table 7-5.
Table 7-5 Inhibitory power of the siloxane ceramic/polymer films

<table>
<thead>
<tr>
<th></th>
<th>CP11-5</th>
<th>CP13-5</th>
<th>CP11-6</th>
<th>CP13-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhibitory Power (%)</td>
<td>71.7</td>
<td>82.5</td>
<td>90.3</td>
<td>93.1</td>
</tr>
</tbody>
</table>

The previous study by Beccaria et al[33] showed the inhibitory powers of their siloxane films were between 60% and 70%. The HCLCoat11 and HCLCoat13 coatings developed by the Hawaii Corrosion Laboratory can be concluded to have an excellent corrosion inhibitory power.

7.3 CERAMIC/POLYMER FILM DEGRADATION

In the last paragraph of the previous section, it was mentioned that the HCLCoat13 film could impede the corrosion occurrence more than the HCLCoat11 film. However, from the results of the morphological change investigation in the chapter 6, the CP13 coupons seemed to have more film degradation than the CP11 coupons. It is assumed that the HCLCoat13 film degraded faster than the HCLCoat11 in seawater. Beccaria et al also suggested that in the Al-siloxane film, the number of defects increased and delamination occurred during sodium chloride solution immersion[33]. Therefore, the degradation mechanism of the HCLCoat11 and the HCLCoat13 films will be discussed in this section.

7.3.1 HCLCoat11 Film Degradation

The HCLCoat11 coating is a quasi-ceramic coating that has little to no hydrocarbons in its structure. It is assumed that the main mechanism of the HCLCoat11 film degradation in seawater could be the structure relaxation of Si-O-Si linkages. The structure relaxation of Si-O-Si linkages is caused by water diffusion and the water
diffuses as molecular water which later reacts with the glass network to form immobile hydroxyls by $H_2O + Si - O - Si \equiv \equiv SiOH + HOSi \equiv [34-36]$. Therefore, the time of the HCLCoat11 film degradation will be estimated using the water diffusion coefficient into silica glass.

The water diffusion coefficient into silica glass is estimated to be $1.0 \times 10^{-16} \text{cm}^2/\text{s}[37]$. Similarly to the penetration time of chloride ion diffusion explained in the section 7.1.1, the penetration time of water molecular diffusion is determined to be $5.00 \times 10^7 \text{seconds}$ which is 579 days, indicating that it could take 579 days for the seawater to break down the HCLCoat11 film. In this study, since the maximum immersion term was 243 days, it is assumed that the HCLCoat11 film did not completely break for all CP11 coupons. The investigation by optical microscopy in chapter 6 confirmed that the HCLCoat11 film of all CP11 coupons did not break down.

Although the film did not break down, the structure relaxation on the surface of the HCLCoat11 film should occur. In order to corroborate that the structure relaxation of Si-O-Si linkages was caused by water diffusion, the change of chemical structure of the film was investigated with Raman spectroscopy. Raman spectra were obtained with a Raman system (wavelength: 532nm, laser power: 36mW). Each spectrum was the average of 5 spectra obtained in 60s exposure time. The Raman bands of each immersion test are shown in Figure 7-13 through Figure 7-16. The left graph of each figure is short range of between 300 and 1900 cm$^{-1}$ and the right of each figure is wide range of between 300 and 3800 cm$^{-1}$.

The Raman bands near 430, 800, 1060, and 1200 cm$^{-1}$ are fundamental vibrations of the dry SiO$_2$ glass framework and the Raman bands of around 970 and 3700 cm$^{-1}$ are
Si-OH stretching mode[38]. Moreover, according to other literature, siloxane ceramic/polymer coatings have several typical Raman bands. They are 2800-3000cm\(^{-1}\) (C-H stretching), 1450cm\(^{-1}\) (H-C-H scissors), 1300cm\(^{-1}\) (H-C-H twist), 980cm\(^{-1}\) (Si-OH stretching), and 3400cm\(^{-1}\) (Si-OH stretching)[8].

From the all short range figures, it is found that the HCLCoat11 film before immersion had the Si-O breathing of 470cm\(^{-1}\), the Si-O stretching of 790cm\(^{-1}\), the H-C-H twist of 1270cm\(^{-1}\), H-C-H scissors of 1420cm\(^{-1}\), and 1200cm\(^{-1}\). It is also found that the HCLCoat11 film before immersion had the C-H stretching of 2800-3000cm\(^{-1}\) from the wide range figures. Although there the Si-OH stretching of 980cm\(^{-1}\) was not found in a cold deep seawater immersion test coupon since immersion time was short, the Si-OH stretching bands were found in artificial seawater, intertidal, and warm surface seawater immersion test coupons. These results support the structure relaxation of Si-O-Si linkages of the HCLCoat11 film by the seawater immersion; consequently, it can be concluded that seawater made the HCLCoat11 film degrade, resulting from the structure relaxation by the water diffusion; however, it would take more immersion time for seawater to break down the entire film.
Figure 7-13 Raman bands (left: 300-1900cm\(^{-1}\), right: 300-3800cm\(^{-1}\)) of artificial ASTM seawater immersion CP11 coupons

Figure 7-14 Raman bands (left: 300-1900cm\(^{-1}\), right: 300-3800cm\(^{-1}\)) of intertidal immersion CP11 coupons

Figure 7-15 Raman bands (left: 300-1900cm\(^{-1}\), right: 300-3800cm\(^{-1}\)) of warm surface seawater immersion CP11 coupons
7.3.2 HCLCoat13 Film Degradation

The HCLCoat13 coating is formulated to incorporate more hydrocarbons than the HCLCoat11 coating to improve adhesion to surfaces with less active functionalities. Therefore, it is assumed that the HCLCoat13 film degradation was caused not only by the structure relaxation of the Si-O-Si linkages but also by the chemical structure change of the organic components of the film. From the investigation with optical microscopy in Chapter 6, it was found that seawater immersion made the HCLCoat13 film break down; especially, the film significantly crazed and delaminated at the edges of the coupons. Since this degradation was observed for only the CP13 coupons and not the CP11 coupons, the chemical structure change of its organic parts was considered the result of this degradation. Therefore, similar to the investigation of the HCLCoat11 film degradation, the change of chemical structure of the HCLCoat13 film was investigated with Raman spectroscopy.

The Raman bands of each immersion test are shown in Figure 7-17 through Figure 7-20. Compared to the Raman bands of the HCLCoat11 film, the Raman spectra
of a few CP13 coupons after immersion were unstable. This is assumed to result of severe film degradation.

For the Raman bands before immersion, the HCLCoat13 had obvious Raman bands which were the Si-O breathing of 470cm\(^{-1}\), the H-C-H twist of 1300cm\(^{-1}\), the H-C-H scissors of 1450cm\(^{-1}\), the C-H stretching of 2800-3000cm\(^{-1}\), the Si-OH stretching of 3400cm\(^{-1}\), and other bands: 640, 1110, 1200, and 1610cm\(^{-1}\). The different bands between before and after immersions were 860cm\(^{-1}\) except the cold deep seawater immersion test. The Raman band of 860cm\(^{-1}\) was considered to be caused by C-H-S bonds[39]. Judging from the fact that the film did not break down for the cold deep seawater immersion test while the film broke down for the other immersion test, (although the mechanism of the C-H-S bond formation from the HCLCoat13 film needs studying,) it can be concluded that the C-H-S bonds formation maybe a key factor in the degradation of the film in seawater. The lack of film degradation in the cold deep seawater immersion test was assumed to be due to the short immersion time.

Figure 7-17 Raman bands (left: 300-1900cm\(^{-1}\), right: 300-3800cm\(^{-1}\)) of artificial ASTM seawater immersion CP13 coupons
Figure 7-18 Raman bands (left: 300-1900cm$^{-1}$, right: 300-3800cm$^{-1}$) of intertidal immersion CP13 coupons

Figure 7-19 Raman bands (left: 300-1900cm$^{-1}$, right: 300-3800cm$^{-1}$) of warm surface seawater immersion CP13 coupons

Figure 7-20 Raman bands (left: 300-1900cm$^{-1}$, right: 300-3800cm$^{-1}$) of cold deep seawater immersion CP13 coupons
7.4 MACROFOULING

Marine organisms thrived on coupons in the intertidal immersion and the warm surface seawater immersion tests at Coconut Island. This is called “macrofouling” and can impair and degrade underwater surfaces of equipment. Organisms such as bacteria, protozoans, algae, and crustaceans can accumulate in large numbers on surfaces like pipes, tanks, and ship hulls, resulting in corrosion, clogging, contamination, or a decrease in the efficiency of moving parts. Hence, anti-fouling effectiveness is one of the most important functions for marine coatings. Notice the significant increase in macrofouling as exposure time increased for both intertidal (Figure 7-21) and continuous immersion (Figure 7-22). In the intertidal immersion tests, the CP11 coupons displayed excellent anti-fouling characteristics (sixth column from the left side of the rack in Figure 7-21). There was significantly more macrofouling in the continuous immersion test where the coupons were exposed to quiescent water. In Figure 7-22, although most of the coupons were covered with marine life, the CP11 coupons were the easiest to clean as the marine life which could not get strong anchoring points on HCLCoat11. This demonstrated the anti-fouling properties of HCLCoat11.
Anti-fouling coatings consists of self-polishing copolymer coatings (SPC) that release biocides and fouling release coatings (FRCs) that prevent adhesion of marine life. The SPC technique employs a heavy metal with the anti fouling tributyltin (TBT) to deter growth of marine organisms. The International Maritime Organization (IMO)
banned development of tributyltin (TBT) in 2001. Thus, one of the modern approaches to anti-fouling coatings is the environmentally friendly FRCs[40].

The siloxane ceramic/polymer coatings (i.e., HCLCoat11 and HCLCoat13) in this study are not biocidal coatings which contain metal or organic compounds toxic to fouling entities. Thus, it is assumed that the HCLCoat11 film has the functions as an FRCs. In order to confirm this assumption, the fouling rate (FR) was determined for the warm surface seawater immersion test coupons after the initial coupon cleaning, similar to the determination of the corrosion-damaged area fraction (section 6.6). An FR of 100 indicates a surface free of macrofouling. The raw images and the binary images of highlighting the macrofouling (black regions indicate macrofouling) is shown in Figure 7-23. The FR is determined with the area fraction of the black region in the binary images. The FRs of the coupons are shown in Table 7-6. The FRs were determined from one coupon of each coupon type. As these results showed, the HCLCoat11 coating definitely has better fouling release than the bare coupons and the other coatings. Comparing the FRs to those of other studies, the FRs of the HCLCoat11(99.8%) coating was greater than those of polysiloxanes coatings that had FRs of 70(not including slime coverage)for 85days immersion[41].

![Figure 7-23 Raw and binary images of macrofouling](image-url)
Table 7-6 Fouling rates of coupons

<table>
<thead>
<tr>
<th></th>
<th>BR</th>
<th>CP11</th>
<th>CP13</th>
<th>ES</th>
<th>PS</th>
<th>EC</th>
<th>PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR [%]</td>
<td>28.61</td>
<td>99.84</td>
<td>52.14</td>
<td>92.42</td>
<td>54.52</td>
<td>38.99</td>
<td>27.51</td>
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According to Choi et al[41], the surface energy is an important factor for fouling release performance. A pristine siloxane sol-gel coating had 80±3° of water contact angle, while a pristine polyurethane coating had only 48±4° of water contact angle[22]. This coincides with the results that the HCLCoat11 coating had more foul release function than the other organic coating.
8 CONCLUSIONS

The siloxane ceramic/polymer coatings (i.e., HCLCoat11 and HCLCoat13) developed in the Hawaii Corrosion Laboratory had excellent corrosion resistance in marine environments as determined using polarization tests and immersion tests. Moreover, it was found that the two coatings had different corrosion behavior and advantages and disadvantages.

The HCLCoat11 film can mitigate the corrosion current density on bare aluminum alloys (Al5052-H3 and Al6061-T6) by 90%. The HCLCoat11 film had many tiny preexisting breaches (pores) whose diameters were 1-2µm, resulting in cathodic corrosion initiation at the breaches at the open-circuit potential. HCLCoat11 film, however, does not apparently degrade in seawater, indicating that the film itself is durable in marine environments since the structure relaxation of Si-O-Si linkages by water molecules requires more time than the eight months of exposure conducted in this research. In addition, HCLCoat11 has excellent fouling release properties, in comparison to the HCLCoat13 coating or the epoxy and polyurethane organic coatings.

The HCLCoat13 film had very little preexisting breaches in comparison to HCLCoat11. In addition, the preexisting breaches on HCLCoat13 had diameters less than 1µm. This resulted in the HCLCoat13 film showing better corrosion resistance than the HCLCoat11 film during the short term polarization experiments. However, the long term seawater immersion showed that the HCLCoat13 broke down resulting in much corrosion compared to coupons coated with HCLCoat11. The degradation of the HCLCoat13 could be due to the C-H-S bond formation by the seawater immersion.
As candidate materials for marine construction such as the heat exchanger of an OTEC plant, the HCLCoat11-coated Al5052-H3 combination was considered to be the best among the bare alloys (i.e., Al5052-H3 and Al6061-T6) and the six coating schemes (list schemes) on Al5052-H3 and Al6061-T6 aluminum alloy substrates based on corrosion barrier durability and fouling release properties.
9 REFERENCE


