

Surface Treatment to Mitigate Exfoliation Corrosion of 5XXX Series Aluminum Alloys

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ABSTRACT

The United States Navy has an urgent need for fast, light-weight ships, such as the Littoral Combat Ship (LCS), which uses strong, ductile, and corrosion-resistant aluminum alloys, AA5083 (UNS A95083) or AA5XXX alloys. Magnesium rich AA5XXX series are susceptible to sensitization that potentially leads to exfoliation (EC) and intergranular corrosion (IGC) when operating conditions exceed 50°C. In order to mitigate exfoliation corrosion, Oceanit has developed and demonstrated an innovative surface treatment approach. A proprietary nanocomposite material was used that resulted in a low energy surface with water contact angle >100° and inert to extreme corrosive chemicals and high temperatures. Through ASTM G66 and B117, testing it was clearly demonstrated that untreated samples exhibited high surface pitting and exfoliated edges whereas the nanocomposite treated sample was near pristine. Microstructural analysis revealed that secondary phase precipitates that are formed and migrated to grain-boundaries on untreated samples, whereas treated samples showed negligible secondary phase precipitates. Based on microscopy and ASTM G66 test results, Oceanit concludes that the nanocomposite treatment offers significant protection in corrosive environments and reduces susceptibility for exfoliation.

Key words: Exfoliation corrosion, aluminum alloy, ASTM G66, nanocomposite, surface treatment, low surface energy coating

INTRODUCTION

Strong, ductile, and corrosion-resistant aluminum alloys, AA5083 (UNS A95083) as well as other AA5XXX alloys have demonstrated properties that are well-suited for marine applications. However, AA5XXX alloys are susceptible to sensitization in which Mg diffuses from the bulk to grain boundaries (Figure 1). This results in β -phase (Al_3Mg_2) formation that makes these alloys vulnerable to exfoliation corrosion, intergranular corrosion (IGC) and stress corrosion cracking (SCC).¹ With a corrosion potential of around -1.29V (SCE), the β -phase is typically more active than the 5083 Al matrix, which has a potential of -0.73V (SCE). The β -phase is thus, preferentially attacked by corrosive environments, which results in anodic dissolution of β -phase from the grain boundaries.

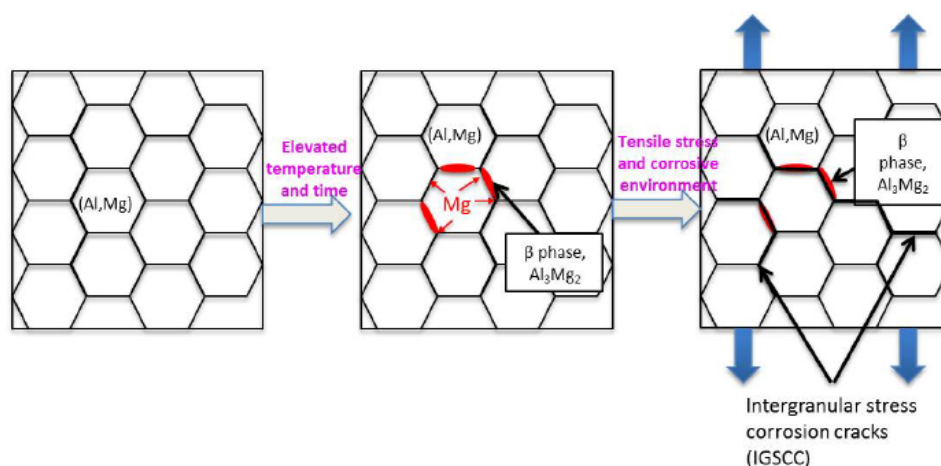


Figure 1: Schematic showing mechanism of intergranular stress corrosion cracking occurs in sensitized Al-Mg alloys.

Aluminum (5xxx series) is a corrosion resistant, high strength alloy commonly employed in ships and marine structures. The 5xxx series has a high magnesium content (>3wt%) and has been shown to be susceptible to sensitization leading to stress cracking, corrosion and exfoliation when operating conditions exceed 50°C. Exfoliation corrosion is a more severe form of intergranular corrosion that can occur along aluminum grain. These grain boundaries in both aluminum sheet and plate are oriented in layers parallel to the surface of the material, due to the rolling process.²

This delamination with white corrosion products between the layers, characterizes exfoliation corrosion.³ In use, the principal danger lies in the potential loss of effective cross section. There are number of different approaches currently pursued to mitigate exfoliation corrosion in aluminum 5XXX. One approach uses ultrasonic impact treatment (UIT) to treat 5456-H116 to mitigate crack initiation and propagation. While shown to be promising, the effects of UIT on the properties and microstructure of 5456-H116 are not well understood. A second approach for reducing corrosion cracking on marine vessels is applying paints and coatings or surface treatments. This method is currently in use but provides minimal protection and must be used in addition to other protective methods. While there are number of coating and surface treatment technologies that offer sufficient protection to aluminum alloys, weight, thickness and overall compatibility of the coatings needs to be fully understood.

In order to address the exfoliation corrosion in aluminum 5XXX, a low surface energy nanocomposite coating “EverPel” was tested using standard coating characterization, exfoliation and accelerated corrosion testing. In addition to the accelerated testing, in depth microscopic analysis was performed on heat-treated samples under different temperature conditions (65, and 150°C) and with nanocomposite coating. The results of the exfoliation corrosion testing and microscopic analysis are presented.

EXPERIMENTAL PROCEDURE

Aluminum 5XXX series 5083-H113 was procured from commercial vendor and cut to desired shapes for various testing. In terms of the coating application, aluminum coupons were cleaned, degreased and a proprietary low surface energy nanocomposite treatment was applied using a spray coating process. The coated substrates were dried at ambient temperature for at least 24 hours before proceeding to characterization. The following tests were conducted to verify the coating's properties.

- (i) Water Contact Angle measurements: A Rame-Hart goniometer was used to measure water contact angle at room temperature.
- (ii) Dry Film Thickness (DFT): A commercial DFT probe was used to determine the coating thickness.
- (iii) ASTM G66: Exfoliation testing were carried out according to ASTM G66 - Standard Test Method for Visual Assessment of Exfoliation Corrosion Susceptibility of 5XXX Series Aluminum Alloys (ASSET Test).

Sample Preparation:

Samples were prepared by degreasing in hexane solution, followed by etching in 5wt% sodium hydroxide at 80°C (176°F) for 1 minute. The samples were removed from sodium hydroxide solution, rinsed in water and de-smutted in concentrated nitric acid for 30 seconds. Finally, the samples were rinsed in deionized water and air-dried.

ASSET Test Solution Immersion:

In order to initiate exfoliation, the aluminum samples were immersed in a test solution. Test solution was prepared by dissolving 53.5 g ammonium chloride (NH_4Cl), 20.0 g ammonium nitrate, (NH_4NO_3) and 1.8 g ammonium tartrate ($(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$) in ~200mL of deionized water in a 1 L beaker. Immediately before the beginning of the experiment, 10mL of 30% hydrogen peroxide was added and the solution was made up to 1L using deionized water. Samples were placed in a plastic container (~125mL) filled with the test solution, capped and placed in a water bath set at 65°C for 24 hours. After 24 hours the samples were removed, rinsed in deionized water and dried. The degree of exfoliation was determined through visual assessment of samples before and after exposure to ASSET test.

- (iv) ASTM B117: Salt Fog Exposure – A standard accelerated salt fog exposure study was carried out on coated and uncoated aluminum substrates following ASTM B117.
- (v) Microscopic Analysis: Optical microscope (OM) and scanning electron microscope (SEM) characterization of selected samples were conducted at University of Illinois, Chicago. Sample preparation involves slicing samples to ~1 x 5 x 5mm and embedding in an epoxy resin. The resin was cured and resulting block was polished using silica powder to obtain a smooth flat surface (Figure 2). Some samples were etched in ammonium persulfate solution to visualize beta phase migration towards to the grain boundaries. In addition to SEM, Energy Dispersive X-Ray Analysis (EDX) was also conducted on select regions of the test sample.