

VAPOR PHASE INHIBITORS TO EXTEND THE LIFE OF AGING AIRCRAFT

Behzad Bavarian, Lisa Reiner, Hamed Youssefpour
Dept. of Manufacturing Systems Engineering & Management
College of Engineering and Computer Science
California State University, Northridge, USA

and

Ivan Juraga
University of Zagreb
Zagreb, Croatia

ABSTRACT

Localized corrosion of aluminum alloys in the aircraft industry can cause expensive catastrophic failures, especially in aging aircraft. To further aggravate conditions, aircraft maintenance with conventional cleaning solutions can gradually destroy the protective aluminum oxide film and accelerate corrosion in crevices and lap joints. A new solution with corrosion inhibition properties used for washing/rinsing aircraft was investigated to determine the corrosion susceptibility for several aluminum alloys. The inhibitor chemical composition, as determined from XPS analysis, is a mixture of sodium compounds and hydrocarbon surfactant with uniform chemistry across the surface and minor variation of concentration with depth. Inhibitor effectiveness was confirmed with EIS and elevated temperature studies. Polarization resistance increased with concentration of inhibitor due to film formation and displacement of water molecules. Cyclic polarization behavior for samples in the vapor phase inhibitor showed a shift in the passive film breakdown potential by roughly +600 mV. The substantial increase in the passivation range has favorable consequences for pitting and localized cell chemistry. The strain at failure and tensile strength from the stress corrosion cracking studies showed pronounced effects at -300 mV; the fractographs showed an improved morphology with ductile overload as the primary failure mode.

Keywords: SCC, vapor phase inhibitors, aging aircraft, aluminum alloys

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INTRODUCTION

One of the major concerns for the airline industry is maintaining this aging fleet of aircraft beyond their design life of 20 years. According to data presented in the 1999 edition of the Aviation & Aerospace Almanac, close to 7500 aircraft were operated by U.S. airlines in 1998 [1]. Some of these aircraft (B-727, DC-10) have been in service since the 1960s, when minimal attention was paid to corrosion. For the aircraft manufactured in the 1970s and 1980s, some corrosion control had been incorporated into the aircraft design (B-737, MD-81 and F-100), but damage tolerance was the primary concern. As the years passed, aircraft corrosion was becoming an economic burden and even endangering structural integrity. As part of the durability standards, airframe manufacturers began to use corrosion inhibiting primers and sealants for the faying surfaces of lap joints and fastener holes. Moreover, the Federal Aviation Administration (FAA) issued Airworthiness Directives (AD) related to corrosion control in design and maintenance [2]. By 1996, the total annual cost of corrosion for the U.S. aircraft industry was estimated at \$2.25 billion; further itemization shows that design and manufacturing cost \$0.25 billion, corrosion maintenance costs \$1.7 billion, and downtime due to corrosion was \$0.3 billion. With the availability of new corrosion resistant materials and an increased awareness of the impact of corrosion on the integrity and operation of jet aircraft, the current design life of 20 years can be extended without jeopardizing structural integrity and significantly increasing the cost of operations. Yet there is still reluctance to use the new materials in aircraft designs.

The primary use of high strength aluminum alloys is in aircraft construction; the airframe of modern aircraft is approximately 80 percent aluminum by weight [3, 4]. Some of the main reasons for selecting an alloy for aircraft applications are corrosion resistance, cost and appearance. Traditionally, the structural aluminum alloys in aircraft have been 2024 in damage critical areas and 7075 in strength critical areas [5, 6]. In the past, when the aircraft was constructed largely of metal, skins were very thin and systems were rapidly replaced due to obsolescence, SCC problems were rare. However, when aircraft structures became more complex and skin materials became integral parts of the structure, SCC became more prevalent. The high performance aircraft designed since 1945 have made extensive use of skin structures machined from thick plates and extrusions. The residual stresses induced by the heat treatment in conjunction with those from the machining process made these materials sensitive to SCC. Maintenance requirements increased as a result and development of higher strength alloys with improved resistance to corrosion began. Aluminum alloys 7075-T6 and 2024-T3 (susceptible to both corrosion and SCC) are commonly used despite the availability of more corrosion resistant aluminum alloys with equal strength and fatigue properties [2].

The heat treatment or natural aging of materials induces residual stresses in these susceptible alloys that combine with operational loading stresses. A structure that has SCC sensitivity, if subjected to stresses and then exposed to a corrosive environment, may initiate cracks and crack growth well below the yield strength of the metal. Consequently, no corrosion products are visible, making it difficult to detect or prevent; fine cracks can penetrate deeply into the part. In Al-alloys and low-carbon steels, intergranular fracture is common. Aluminum alloys that contain appreciable amounts of soluble copper, magnesium, silicon and zinc are susceptible to SCC [7, 8]. The service record of 6000 series aluminum alloys shows no reported cases of SCC. In laboratory tests, however, at high stresses and in aggressive solutions, cracking has been demonstrated for particularly high silicon or copper content. Traditionally, corrosion has not been given sufficient attention with respect to structural integrity, possibly due to complexities of the corrosion process and the inability to predict nucleation and growth behavior. Corrosion has not been incorporated into the damage tolerance assessments and as aircraft continue to age, corrosion will increasingly affect the structural integrity [2].

Vapor phase corrosion inhibitors

Several groups of organic compounds have reported inhibitive effects for aluminum corrosion. The extent of adsorption of an inhibitor depends on many factors: (a) the nature and the surface charge of the metal; (b) the inhibitor adsorption mode; and (c) the inhibitor's chemical structure. The presence of heteroatoms (oxygen, nitrogen, sulfur, phosphorus), triple bonds and aromatic rings in the inhibitor's chemical structure enhance the adsorption process [9]. Coating to substrate adhesion and the diffusion of water and other species from an external environment to the coating/substrate interface are critical factors for the corrosion inhibition of organic protective coatings. A possibility for aircraft protection is Volatile Corrosion Inhibitors (VCI), where protective vapors deposit on the exposed surfaces (including cracks and crevices) and condense to form a thin barrier of tiny crystals. The crystals dissolve when in contact with water, causing the adsorption of a monomolecular coating to the metal surface that helps repel water. VCI can also neutralize pH, which is an effective way to adjust the localized chemistry inside a crevice, pit or crack.

VCI is often a complex mixture of amine salts and aromatic sulfonic acids that provide direct contact inhibition and incorporate volatile carboxylic acid salts as a vapor phase inhibitor for metal surfaces not sufficiently coated. The thin polar layer of surfactants is tightly bound to the metal surface through chemisorption. Between this thin polar layer and the corrosive environment is the thicker barrier layer of hydrocarbons. The sulfonate part of the inhibitor displaces water from the metal and is chemisorbed to the surface [10]. A surface active inhibitor component will be strongly chemisorbed or adsorbed at active sites having energy levels complimentary to the energy levels of the polar group, thereby forming a tighter, more uniform layer over the metal surface. The barrier layer has three important characteristics: 1) low permeability by moisture and other corrosives; 2) compatibility with the oleophilic ends of the polar layer molecules so that the barrier is held firmly in place; and 3) good solubility in the carrier to attach the polar and barrier layers to the metal surface [10]. The VCI film barrier replenishes through further evaporation and condensation of the inhibitor on the metal surface.

Aircraft maintenance

Aircraft components are frequently washed or rinsed during manufacturing and while in service to remove contaminants (salt, dirt, grease and oil). There are three main types of cleaning: aqueous, organic solvent, and abrasive. Aqueous cleaning covers a wide variety of cleaning methods (detergents, acids and alkaline compounds) to displace soil. Improved corrosion prevention compounds and coating systems can isolate the sensitive alloy from the environment. These coatings, combined with improved repair and maintenance procedures, will ensure adequate performance of a structure manufactured from a SCC sensitive alloy. The most costly, yet best method for eliminating SCC is to replace the material with an alloy specifically designed to resist this form of corrosion. The new aircraft wash inhibitor investigated in this program is a heavy duty, biodegradable, water based alkaline cleaner and degreaser. The compounds function by altering hydrocarbons (grease) so that the deposits can be removed with water. Any conventional equipment (power washers, steam cleaners, dip tanks) can be used for multimetal corrosion protection. Ethoxylated alcohols (C₉-C₁₁), the active ingredient in the inhibitor are based on short chain alcohols giving fast penetration of soil and improved performance on hard surfaces.

Stress Corrosion Cracking

The slow strain rate tests showed that the protection afforded by the inhibitor is more noticeable in the higher anodic potential range. Susceptibility to SCC was determined for the three alloys. At potentials exceeding breakdown, a noticeable increase in susceptibility is seen for the samples tested without inhibitor (Figures 2-4). The greatest reduction in degree of susceptibility is seen around 300mV. Tables 2-4 show some of the SEM photographs from these SCC testing. These micrographs demonstrate greater susceptibility to SCC for samples tested in solution without inhibitor. Examination of the failed samples revealed some damage for all Aluminum alloys in both testing conditions at the more aggressive potentials (-300 mV and -400 mV). For Al-6061, SCC attack was seen at all potential levels for the untreated specimen, however very minor damage at -700 mV. The SEM photos for Al-7075 showed minor levels of SCC attack and pitting corrosion at the edges. In general, the morphology of the samples tested in tap water showed more intergranular attacks. Samples tested in the new VCI wash solution showed a typical ductile overload failure with no localized corrosion damage except at aggressive anodic potentials higher than -300 mV.

Verification of the Inhibitor Mechanism

To explore the activation energy of the corrosion process and the adsorption thermodynamics for the new VCI wash solution, cyclic polarization was conducted in temperatures ranging from 35°C to 55°C. Corresponding data are given in Table 5 and demonstrate the temperature dependence of I_{corr} and E_{corr} obtained in 2000 ppm VCI and 3.5% solution with deionized water. The results show that the corrosion behavior of aluminum 7075 fluctuates with temperature. The increased temperature causes a more negative E_{corr} and also increases the I_{corr} . EIS, when modeled correctly, is a powerful tool for the analysis of complex electrochemical systems. A modified Randles model was used to obtain the polarization resistance (R_p) values. The Bode plots show that VCI increases the polarization resistance of the Al-alloy samples (Figures 5-7) with higher inhibitor concentrations resulting in higher R_p values. The increased polarization resistance can be attributed to the film formation on the aluminum surfaces. The addition of inhibitor has increased the R_p value from 6 k Ω for Al-7075 in the blank solution (0 ppm concentration) to 134 k Ω for 5000 ppm VCI in solution (Table 6). For Al-6061, the increase is from 11 k Ω to 58 k Ω for 3000 ppm and for Al-2024, the increase was from 16.7 k Ω to 597 k Ω for 5000 ppm.

The data acquired from the EIS tests show that VCI increases the polarization resistance (R_p) value. It is assumed that the extremely high R_p value (in the range of a hundred thousand ohms) is due to the progressive film formation on aluminum. The data obtained from the EIS experiment best fit the Langmuir adsorption isotherm, where $\ln C$ vs. $[\ln \theta - \ln (1-\theta)]$ resulted in good linearity as seen in Figure 6. The thermodynamics of adsorption can provide valuable information about the mechanism of inhibition. The important thermodynamic values (changes in enthalpy of adsorption and changes in free standard energy of adsorption) can be obtained with adsorption isotherms and classical thermodynamics. The value of ΔG_{ad} is important for the identification of an adsorption mechanism. In chemisorption (chemical adsorption), ΔG_{ad} is usually much higher than physisorption (physical adsorption). The criterion for chemisorption varies, for example, Bridka has suggested that chemisorption requires about -100 kJ/mol energy, whereas Metikos-Hukovic believes that chemisorption needs about -40 kJ/mol energy [14]. Still others assert that physisorption requires energy between -5 to -20 kJ/mol. ΔH_{ad} also plays an important role in the identification of an adsorption mechanism [13]. These analysis on the new aircraft wash showed that the enthalpy of adsorption to be about -37 kJ/mol, which suggest that this product is a chemisorption. Generally chemisorption makes strong bonding between the inhibitor and the surface of the substrate that the inhibitor has been applied to, resulting in more stable protective film.

X-ray Photoelectron Spectroscopy

Samples of 7075-T6 aluminum alloy were coated with VCI inhibitor, air dried for 36 hours and placed in the vacuum chamber of a Kratos Axis Ultra for examination. Figures 9-10 show the XPS analysis (these spectrums were generated using hybrid lens mode, pass energy of 80, Al monochromatic anode, step rate of 1000 m eV, dwell time of 60 ms). Figure 9 shows the VCI chemical composition is a mixture of sodium compounds and hydrocarbon surfactant. Figure 10 shows the same uniform chemistry at different locations; each colored curve represents another scan of the surface. Table 7 provides information for the XPS depth profile beginning at the surface and etching away layers of material for 180 second intervals. At the end of each etch cycle, the composition was determined. The chemical components remain constant throughout the depth profiling, but the surfactant concentration increased slightly with etching (closer to the metal surface). Initially, it was thought the product contained an excess of sodium hydroxide that served as a pH adjuster. Electrochemical test results showed visible evidence of film formation, indicating that this new aircraft wash has dual effects, pH adjusting and film forming that can contribute to improving durability of aircraft structures.

CONCLUSIONS

A comprehensive investigation was undertaken to characterize the corrosion behavior of aircraft aluminum alloys (2024-T3, 6061-T6, 7075-T6) in a vapor phase corrosion inhibitor used as new wash for aircraft. Effectiveness of the inhibitor was confirmed with electrochemical impedance spectroscopy and elevated temperature studies. As well, identification of the adsorption mechanism and corrosion activation energy was explored. The data acquired from EIS tests showed that adsorption of VCI to the high strength aluminum alloys fits with the Langmuir adsorption isotherm and the enthalpy of adsorption to be about -37 kJ/mol, which suggest that this product is a chemisorption compound. XPS analysis showed strong carbon bonding, further corroborating the adsorption isotherm calculations.

Cyclic polarization behavior for samples in the vapor phase inhibitor showed a shift in the passive film breakdown potential by roughly +600 mV. This dramatic increase in the passivation range will reduce pitting and improve localized cell chemistry. Crevice corrosion test results showed improved corrosion inhibition behavior compared with samples tested in tap water only. The strain at failure and tensile strength from the stress corrosion cracking studies showed pronounced effects at -300mV; significant improvements are seen for the samples tested with VCI. Furthermore, ductile overload failure mode was observed for the alloys tested in the inhibitor solution. In summary, this modified new aircraft wash with VCI inhibitor demonstrates to be an effective protective film former on the aluminum alloys with no adverse effects from its alkaline chemistry, and can contribute to improving durability for aircraft structures.

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Table 1 – Crevice corrosion tests on 7075-T6 alloy in Alternate Immersion for 500 Hrs.

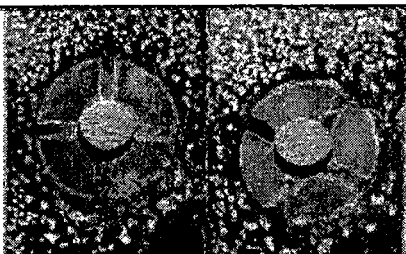



	<p>1% NaCl</p>		<p>5% VCI, Tap water, 1% NaCl</p>
	<p>Tap water</p>		<p>10% VCI, Tap water, 1% NaCl</p>

Table 2 – SEM micrographs of the fracture surface for 2024-T3 after SCC tests in different electrochemical conditions

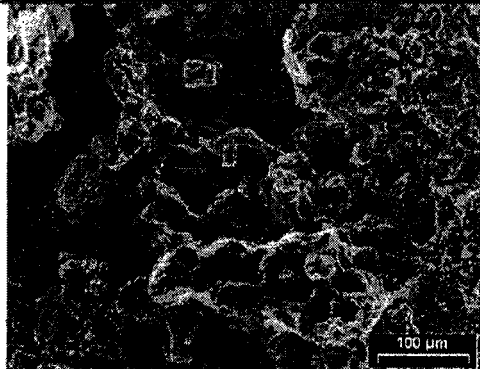
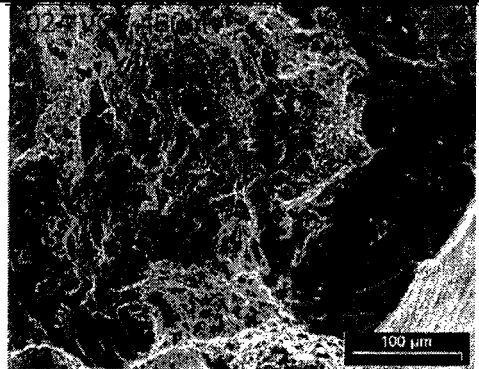
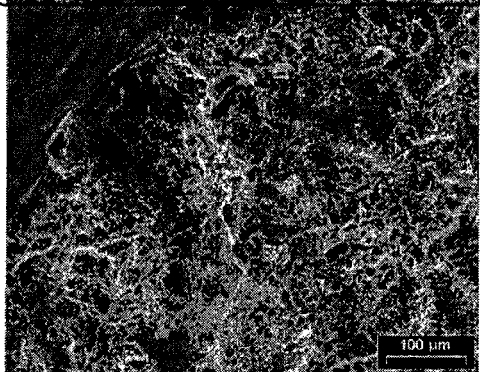
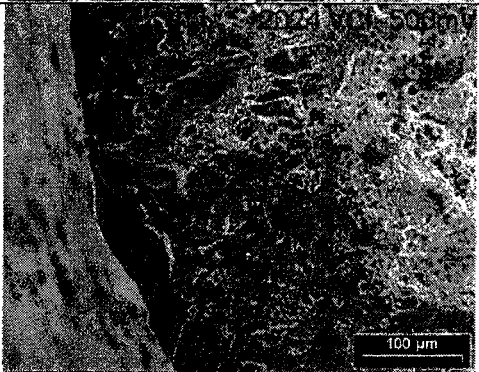

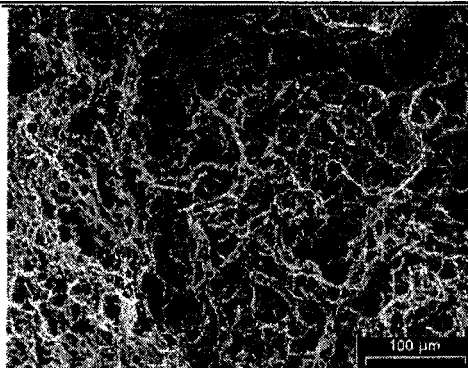
Potential (mV)	Tap water	VCI
-400		
-500		

Table 3 – SEM micrographs of the fracture surface for 6061-T6 after SCC tests in different electrochemical conditions

Potential (mV)	Tap water	VCI
-500		
-600	