Corrosion Inhibition of Stress Corrosion Cracking and Localized Corrosion of Turbo-Expander and Steam/Gas Turbines Materials

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ABSTRACT. Stress corrosion cracking of 7050 aluminum alloys and ASTM A470 steel in the turbo expander and steam/gas turbine industry can cause expensive catastrophic failures, especially for turbo machinery systems performing in hostile, corrosive environments. Commercially available inhibitors were investigated for their effectiveness in reducing and controlling the corrosion susceptibility. Inhibitor effectiveness was confirmed with electrochemical corrosion techniques in different solutions. Polarization resistance increased with concentration of corrosion inhibitor due to film formation and displacement of water molecules. Cyclic polarization behavior for samples in the 1.0% and 5.0% inhibitors showed a shift in the passive film breakdown potential. The substantial increase in the passive range has positive consequences for neutralizing pitting and crevice corrosion cell chemistry. The strain to failure and tensile strength obtained from the slow strain rate studies for both alloys showed pronounced improvement due to corrosion inhibitor ability to mitigate SCC; the fractographic analysis showed a changed morphology with ductile overload as the primary failure mode instead of transgranular or intergranular cracking.

INTRODUCTION

The accumulation of damage due to localized corrosion (pitting, stress corrosion cracking [SCC] and corrosion fatigue [CF]) in low pressure steam turbine components, such as blades, discs and rotors, has consistently been identified as a main cause of turbine failure [1,2]. Accordingly, the development of effective localized corrosion inhibitors is essential for the successful avoidance of unscheduled downtime in steam turbines or other complex industrial and infrastructural systems and for the successful implementation of life extension strategies. Most damage occurs during the shutdown period due to chemistry changes and localized stagnant conditions. The environmental changes during the shutdown period significantly influence the probability of failure for the blades and discs in low pressure steam turbines. [O_2], [Cl^-], temperature, pH, and time spent in shutdown under aerated conditions increase the probability of localized corrosion attacks. Increase in [Cl^-] concentration and pH changes affect the stability of the protective oxides and eventually its breakdown pitting, stress corrosion cracking and corrosion fatigue [3-5].

Vapor phase corrosion inhibitors are often a complex mixture of amine salts and aromatic sulfonic acids that provide direct contact inhibition and incorporate volatile carboxilic acid salts as a vapor phase inhibitor for metal surfaces not sufficiently coated. A surface active inhibitor component will be strongly adsorbed at active sites having energy levels complimentary to the energy levels of the polar group, thereby forming a tighter, more uniform protective layer over the metal surface [6].

EXPERIMENTAL PROCEDURES

Electrochemical polarization tests were conducted (ASTM-G61) to evaluate the effects of these inhibitors on the ASTM A470 steel and 7050 aluminum alloy. The studies were conducted using a Gamry PC4/750™ Potentiostat/Galvanostat/ZRA and DC105 corrosion test software. These alloys were tested in a solution of 1.0% and 5.0% inhibitor plus 200 ppm Cl- solution. Gamry electrochemical impedance spectroscopy EIS300™ systems were used to conduct cyclic polarization tests in temperatures ranging from 20 ^{o}C to 50 ^{o}C and to gather data for adsorption isotherms, tests were conducted in different inhibitor concentrations. The resistance polarization values were used to model adsorption isotherms. Crevice corrosion was conducted on both alloys in an eight-station alternate immersion system. Test were conducted per ASTM G44 and G47 for 200 cycles, the samples were examined and photographed to document their crevice corrosion resistances. The susceptibility to SCC was performed using slow strain rate tests (ASTM G128) under controlled electrochemical conditions using a strain rate of $5x10^{-7}$ sec^{-1}. To determine the degree of inhibitor effectiveness, anodic potentials close to breakdown potentials (-400mV for the 7050 alloy and -200 mV for ASTM A470) were applied.

RESULTS

Electrochemical Polarization Behavior. Electrochemical polarization behavior for two alloys in 200 ppm Cl- and 1.0% or 5.0% VCI inhibitor solutions showed a positive shift in the breakdown potentials by more than 500 mV. The inhibitor altered the electrochemistry, increased the passivation range significantly, and had beneficial consequences for pitting and localized corrosion. The extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range; therefore, corrosion attacks during shutdown period will be minimized.

Crevice Corrosion. Both alloy samples showed significant improvement in resistance to crevice corrosion after 200 hours of alternate immersion in various solutions. The samples immersed in 200 ppm Cl- and 5.0% VCI showed better corrosion resistance. The corrosion damage and discoloration were reduced with the addition of inhibitor for both alloys immersed in 1.0 and 5.0% VCI solutions. The passive film stability has improved the corrosion resistance for the inhibitor treated samples.

Stress Corrosion Cracking. Susceptibility to SCC was determined for both alloys close to their breakdown potentials. A noticeable increase in susceptibility with intergranular cracking modes is seen for the samples tested without inhibitor. The greatest reduction in degree of susceptibility is seen around -200 mV for ASTM A470 and around -400 mV for 7050 samples. Therefore, effectiveness of inhibitors was examined at these applied potentials. The morphology of the samples tested in non-protected solutions showed more intergranular attacks. Samples tested in the presence of VCI inhibitors showed mainly ductile overload failure with less localized corrosion damage. The slow strain rate tests showed that the protection afforded by the inhibitor is noticeable in the active anodic potential range. Both alloys showed a degree of SCC susceptibility of 95% in 5.0% VCI, 84% for 1.0% VCI compared with 45% for unprotected solutions (Figure 1). Corrosion fatigue tests on 7050 Al-alloy showed that the fatigue crack growth rate in the presence of inhibitor is more similar to inert environments. Tests conducted in 5.0% VCI solution showed no evidence of crack arrest effects that were observed in 200 ppm Cl- solution, mainly due to less corrosion product formation.

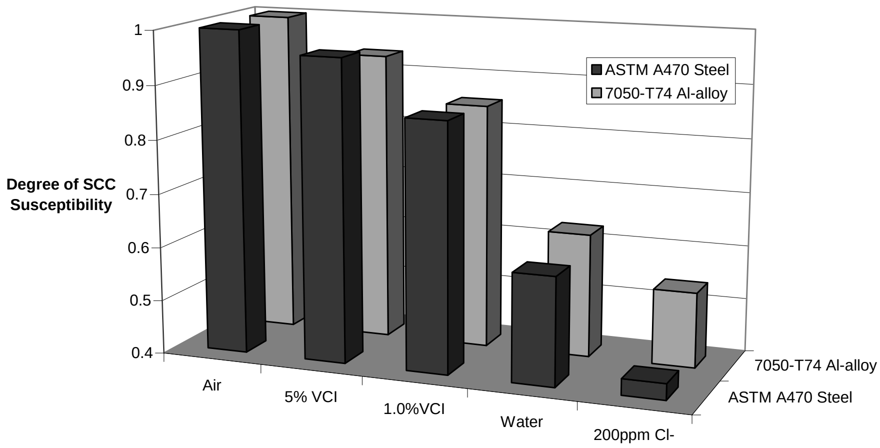
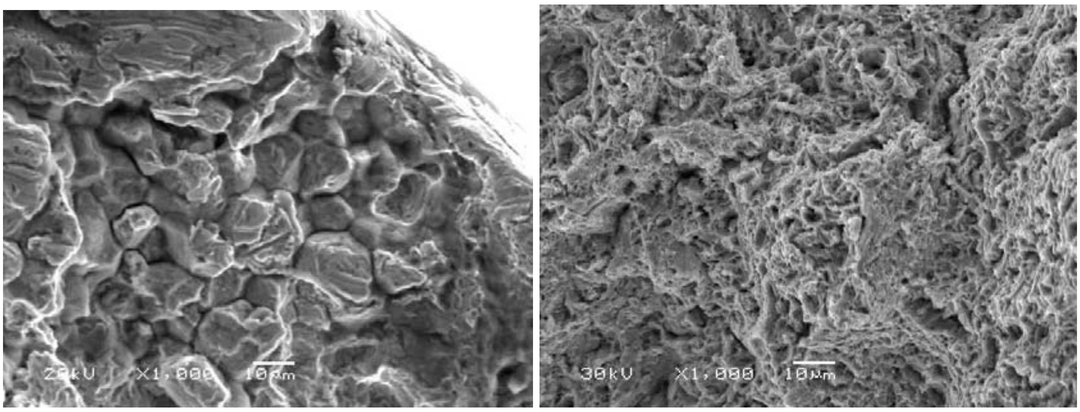


Figure 1: Slow strain rate tests on 7050-T74 Al-alloy (-400 mV_{SCE}) and ASTM A470 (-200 mV_{SCE}) per ASTM G128 in different solutions at $5x10^{-7}$ sec^{-1}.



200ppm Cl- at -200mVsce   200ppm Cl- +5%VCI at -200mVsce

Figure 2: SEM fractographs of ASTM A470 in unprotected and protected condition, showing failure mode changes in SCC tests.

Verification of the Inhibitor Mechanism: To explore the activation energy of the corrosion process and the adsorption thermodynamics, cyclic polarization and EIS were conducted in temperatures ranging from 20°C to 50°C in 1.0% and 5.0% VCI solutions. The results show that the corrosion behavior of both had less fluctuation during EIS tests. Therefore, EIS results and a modified Randles model were used to obtain the polarization resistance (Rp) values. The Bode plots show that VCI increases the polarization resistance of both alloys with higher inhibitor concentrations (Table 1). The addition of inhibitor has increased the Rp value and can be attributed to the film formation on the metal surfaces.

Table 1: Polarization resistance (KΩ) for ASTM A470 aluminum alloys generated by EIS in 200 ppm Cl-.

	VCI Concentration (%)		
Alloy	0.0%	1.0 % VCI	5.0 % VCI
ASTM A470	2.8	220	766
7050-T74	5.4	29	83

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 [7]. Still others assert that physisorption requires energy between -5 to -20 kJ/mol. Analysis of the VCI inhibitor showed that inhibitor adsorption to these alloys surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is roughly between -14 to -18 kJ/mol, which suggests that this product is borderline between a strong physical adsorption or a weak chemical adsorption response with the metal surface.

CONCLUSIONS

A comprehensive investigation was undertaken to characterize the corrosion behavior of turbo machinery systems in vapor phase corrosion inhibitors. Effectiveness of the inhibitor was confirmed with electrochemical impedance spectroscopy at elevated temperature studies. As well, identification of the adsorption mechanism and corrosion activation energy was explored. The data acquired from EIS tests showed that inhibitor adsorption to these alloys surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is about -14 to -18 kJ/mol, suggesting that this product is a relatively strong physical adsorption and weak chemisorption compound.

Cyclic polarization behavior for samples in the vapor phase inhibitor showed a shift in the passive film breakdown potential by roughly +500 mV. This increase in the passivation range will improve localized corrosion resistance. Crevice corrosion test results showed improved corrosion behavior compared with unprotected samples. The stress corrosion studies showed less SCC susceptibility for the samples in VCI inhibitors in the solution. Furthermore, ductile overload failure mode was observed for the alloys tested in the 5.0 % VCI inhibitor solution.

In summary, this investigation demonstrated that the addition of VCI inhibitor to the environment provides effective corrosion protection for both ASTM A470 and 7050 alloys during shutdown period for the blades and discs in low pressure steam turbines.

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