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Electrochemical and SCC Inhibition of Multi-alloy Systems using Vapor Corrosion Inhibitors

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Commercially available inhibitors were successfully investigated for their effectiveness in reducing the corrosion susceptibility of the turbo expander and steam/gas turbine industry alloys. However, due to the fact that the power generating system is complex and consists of a multi-alloy system, the investigation was expanded to study the corrosion behavior and stress corrosion susceptibility of other alloys such as, copper, brass C36000, C69300, red brass C83600, and nickel plated-copper in the presence of these inhibitors. Electrochemical behavior (cyclic polarization and EIS) of these alloys in a 200 ppm chloride solution with different percentages of inhibitor showed significant improvement in passivity, and breakdown potentials. The data acquired from electrochemical tests showed that inhibitor adsorption to the alloy surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is about -10 to -16 kJ/mol, suggesting that this chemical compound provides physisorption to the alloy surfaces. During testing per ASTM(1) standards G44 and G38, no susceptibility to environmentally-assisted cracking was observed upon the addition of 10% inhibitor.

Key words: VCI, SCC, Critical pitting temperature, steam turbine, Volatile corrosion inhibitors, physisorption, brass and copper alloys

INTRODUCTION

Corrosion inhibition of the steam turbine rotor materials in power plants was investigated. It was successfully demonstrated for A470 (class 2 to 7) and ASTM(1) A471 that susceptibility to stress corrosion cracking (SCC), hydrogen embrittlement (HE), and corrosion fatigue (CF) was reduced by using commercially available inhibitors.[1] However, due to the fact that the power generating system is complex and consists of a multi-alloy system, the investigation was expanded to study the corrosion behavior and stress corrosion susceptibility of other alloys such

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[1] ASTM International, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA, 19428

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as, copper and brass alloys including C36000 (38% Zn), Eco-brass C69300 (21% Zn), red brass C83600 (8% Zn), and nickel plated-copper in the presence of these inhibitors. The objective was to verify performance in terms of effectiveness or adverse effects on auxiliary components such as valves, strainer, and heat exchanger caused by the corrosion inhibitors.

Turbo-machinery maintenance

Turbo-machinery systems have regular service maintenance and unexpected shut downs. During scheduled service maintenance, components are frequently washed to dilute or remove any in service 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 protect the sensitive alloys from the environment. These coatings, combined with improved repair and maintenance procedures, will ensure adequate performance of equipment manufactured from a stress corrosion cracking 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 inhibitors investigated in this program are biodegradable compounds that blend amine salts, carboxylic acid, and a wetting agent (surfactant) in a water solution. Wetting agents are added to maintain aminocarboxylates on the metal surface. The compounds alter hydrocarbons (grease) so that the deposits can be removed with water. Any conventional cleaning equipment (power washers, steam cleaners, dip tanks) can be used for multi-metal corrosion protection.

Corrosion inhibitors

Several groups of organic compounds have shown corrosion inhibition properties. Most of the effective organic compounds contain oxygen, sulfur, phosphorus or nitrogen atoms, and in terms of structure, have triple bonds and aromatic rings to improve the inhibitor's adsorption to the metal surface.[2,3] Organic inhibitors can protect by adsorbing to the metal surfaces, molecules attach directly to the surface, in a very thin layer (monomolecular), and do not penetrate into the bulk of the metal. The extent of adsorption of an inhibitor depends on many factors: 1) the nature and the surface charge of the metal; 2) the inhibitor-adsorption mode; and 3) the inhibitor's chemical structure. Volatile corrosion inhibitors (VCI) deposit protective vapors on surfaces, in cracks, pits and crevices, which condense to form a thin barrier film. VCI can also neutralize the pH and other corrosive species, which is an effective way to reduce acidity of the local chemistry inside a turbine system.

Frequently, VCI are a complex mixture of amine salts and aromatic sulfonic acids that provide direct contact inhibition and may incorporate volatile carboxylic acid salts as a vapor inhibitor for metal surfaces not sufficiently coated. The thin polar layer of surfactants is tightly bound to the metal surface through chemisorption or physisorption. 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 surface and promotes adsorption of inhibitor to the surface. Active sites with complementary energy levels to the polar group energy levels form a tighter, more uniform layer over the metal surface. The barrier layer has three important characteristics: 1) low permeability by moisture; 2) compatibility with the oleophillic 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. The VCI film barrier replenishes through further evaporation and condensation of the inhibitor on the metal surface.

VpCI-337(2)(Inhibitor-A) is a ready-to-use waterborne corrosion inhibitor for indoor use. The vapor phase corrosion inhibitors in Inhibitor-A over time migrate and protect metal surfaces, resulting in time and cost savings.

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[2] VpCI-337, Cortec Corp, 4119 White Bear Parkway, St. Paul, MN 55110 U.S.A.

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An adsorption isotherm is a mathematical function that relates the surface coverage of a chemical on a surface (usually a metal) to the concentration of the chemical. Identification of the surface adsorption isotherm is important and can lead to the determination of a mechanism. It is assumed that the corrosion current density, which is directly related to the corrosion rate, is representative of the number of corrosion sites. Therefore, adding inhibitor to the environment should diminish the number of corrosion initiation sites by displacing water molecules on the surface with inhibitor molecules, thereby decreasing the corrosion rate. In recent years, electrochemical and weight loss methods that relate the corrosion current density or the amount of weight loss with the inhibitor coverage have been used to study adsorption and the corrosion inhibition of various materials on a metallic surface.[3,4] Many models for adsorption isotherms have been defined, i.e., Temkin, Freundlich, Langmuir and Frumkin. Each of these adsorption isotherms explains a different type of relationship between the concentration and surface coverage of an inhibitor on a metal or alloy surface.[3-5] Based on the adsorption isotherm graph, the adsorption equilibrium constant, K_{ad}, can be calculated. Identifying the adsorption equilibrium constant, can lead to the calculation of the free standard energy of adsorption, $\Delta G_{ad} = -RT \text{ Ln } (K_{ad})$. By repeating the same experiment at different temperatures, the enthalpy of adsorption, ΔH_{ad} can be calculated.

EXPERIMENTAL PROCEDURE

Corrosion inhibition of Inhibitor-A was investigated for Cu-alloys such as UNS C36000, C69300, and C83600, and Ni-plated copper commonly used in turbo-expander and steam/gas turbine applications. Electrochemical polarization standards per ASTM-G61[6] and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical behavior of this inhibitor on these alloys. These techniques can provide useful information regarding the corrosion mechanisms, corrosion rate and localized corrosion susceptibility of a material in a given environment. The studies were conducted using Gamry(3) PC4/750™ Potentiostat/Galvanostat/ZRA instrumentation and DC105 corrosion test software. Samples were polished (600 grit) placed in a flat cell and tested in different inhibitor concentrations with deionized water and 200 ppm Cl^- solutions. A series of cyclic polarization tests were performed in temperatures ranging from 20°C to 60°C. Gamry's electrochemical impedance spectroscopy (EIS300(4)) software was used to investigate the inhibitor effectiveness on these alloys and gather data for adsorption isotherms in different inhibitor concentrations of deionized water solutions containing 200 ppm Cl^- with. The R_p, polarization resistance value (determined from the Bode plot) was used to fit the data into adsorption isotherm models.

Stress Corrosion Investigation

C-ring samples (ASTM G38) of these alloys were tested in an eight-station alternate immersion system (ASTM G44).[7] The samples were immersed in 10% VCI-A corrosion inhibitor, sodium chloride (Cl^-) and tap water. The applied stress on these C-rings ranges from 60% to 90% of the alloy yield strength. Alternate immersion, an aggressive procedure, was performed to evaluate the inhibitor's ability to retard stress corrosion cracking. The testing cycle for the samples consisted of 10 min immersion and 50 min exposure to air per ASTM G44[7] and G38.[8] After 200 cycles of testing, the samples were disassembled, examined, and photographed to document corrosion resistance.

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[3] Trade name

[4] Trade name

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RESULTS

Cyclic Polarization Behavior

Figure 1 and Table 1 show the polarization behavior for brass C36000 in varying concentrations (0.0% and 10%) of Inhibitor-A with 200 ppm Cl^-, temperatures ranging between 20°C to 50°C. The most noticeable changes are the positive shift in the breakdown potentials and expansion of the passive range for these alloys in Inhibitor-A. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and had beneficial consequences for reducing localized corrosion damages. As demonstrated in these polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film, and shift of the critical pitting potential to higher levels.

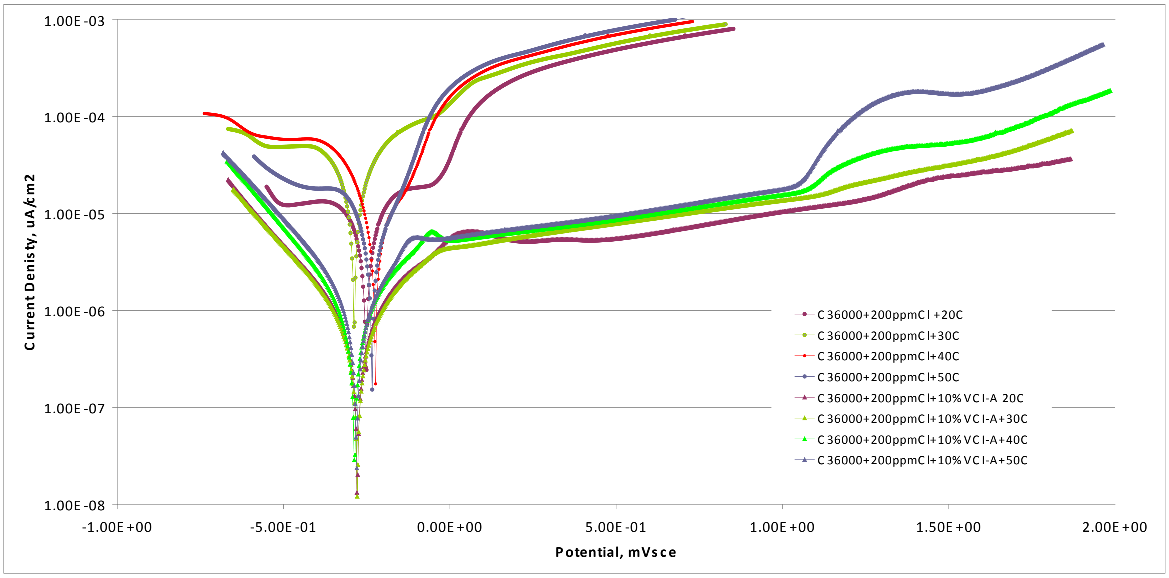

Figure 1: Electrochemical polarization behavior of Brass C36000 in 10% Inhibitor-A with 200 ppm chloride ions at different temperatures.

Table 1

Effects of temperature on electrochemical behavior of C36000 in solution with **200 ppm Cl^- and 10.0% Inhibitor-A.**

Solutions	Temp	Ec	Eb	CR
200 ppm Cl^- +	^oC	mV_{SCE}	mV_{SCE}	uA/cm^2
0.0% Inhibitor-A	20	-250	-37	4.05
10.0% Inhibitor-A	20	-279	+1280	0.30
0.0% Inhibitor-A	30	-285	active	13.40
10.0% Inhibitor-A	30	-279	+1150	0.34
0.0% Inhibitor-A	40	-250	active	13.80
10.0% Inhibitor-A	40	-279	+1090	0.48
0.0% Inhibitor-A	50	-233	active	8.50
10.0% Inhibitor-A	50	-280	+1060	0.62

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Figure 2 shows the polarization behavior for Ni-plated copper in solution with 10% Inhibitor-A and 200 ppm Cl$^-$ at different temperatures (20 to 50°C). These graphs show that the inhibitor has no adverse effect on this material. Table 2 shows the electrochemical behavior of different alloys in different concentrations of inhibitor. Electrochemical impedance spectroscopy, EIS (per ASTM G106) test results are summarized in Table 3 and Figure 2. Inhibitor-A increased the resistance polarization. The increased polarization resistance can be attributed to the film formation on the metal surfaces and its ability to neutralize the corrosive species.

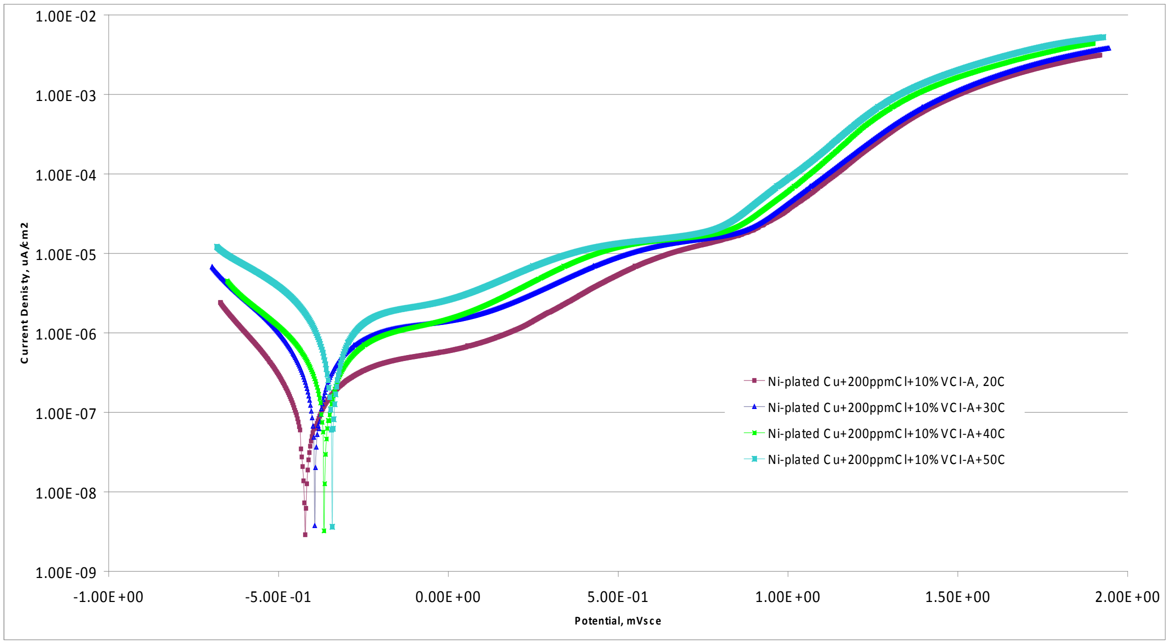

Figure 2: Electrochemical polarization behavior of Ni-plated copper in 10% Inhibitor-A with 200 ppm chloride ions at different temperatures, showing no significant changes

Table 2
Effects of temperature on electrochemical behavior of different alloys in 200 ppm Cl$^-$ and 10.0% Inhibitor-A.

Solutions	Alloy	Ec	Eb	CR
200 ppm Cl$^-$ +		mV$_{SCE}$	mV$_{SCE}$	uA/cm^2
0.0% Inhibitor-A	83600	-241	-114	2.62
10.0% Inhibitor-A	83600	-198	+1340	0.22
0.0% Inhibitor-A	69300	-260	-139	6.40
10.0% Inhibitor-A	69300	-288	+1100	0.78
0.0% Inhibitor-A	Ni-plated Cu	-286	+324	0.11
10.0% Inhibitor-A	Ni-plated Cu	-419	+895	0.13

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Table 3
Rp values for different alloys determined from EIS in different concentrations of Inhibitor-A.

Alloys	Inhibitor-A Concentration (%)		
	0.0%	5.0%	10.0%
	R_p value (Kohms)		
Cu	4.7	1050	1220
Ni-plated Cu	485	4600	4750
C36000	10.7	490	620
C69300	39.3	474	670
C83600	28.7	1600	2180

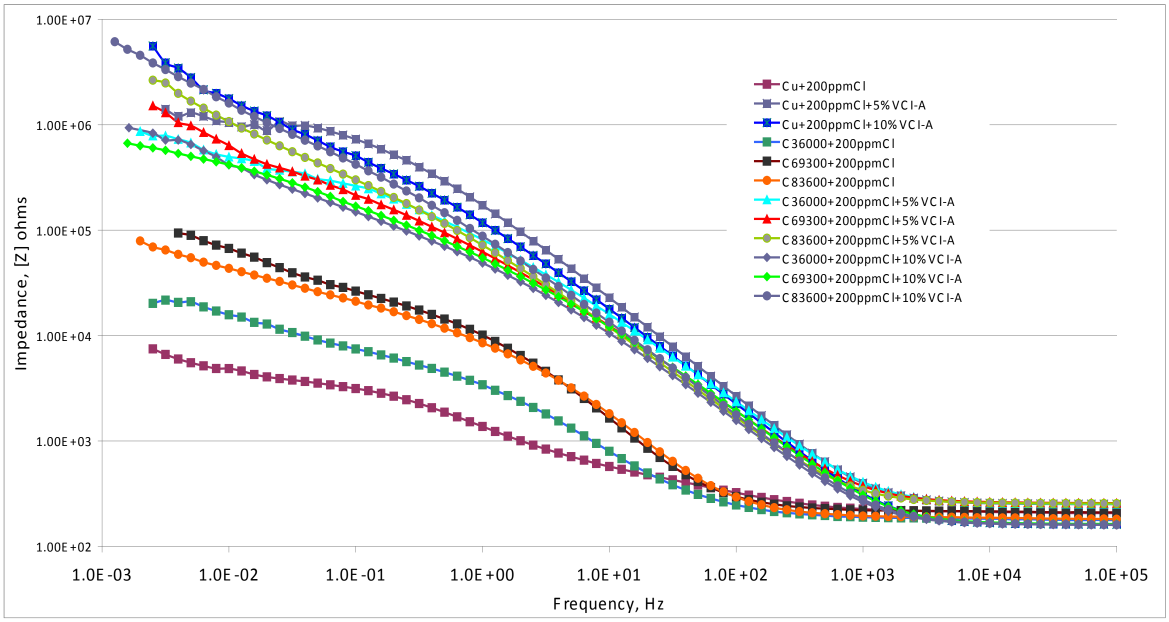

Figure 3: Electrochemical impedance spectroscopy Bode plots for Cu, C36000, C69300 and C83600 brass in solutions with **different Inhibitor-A concentrations.**

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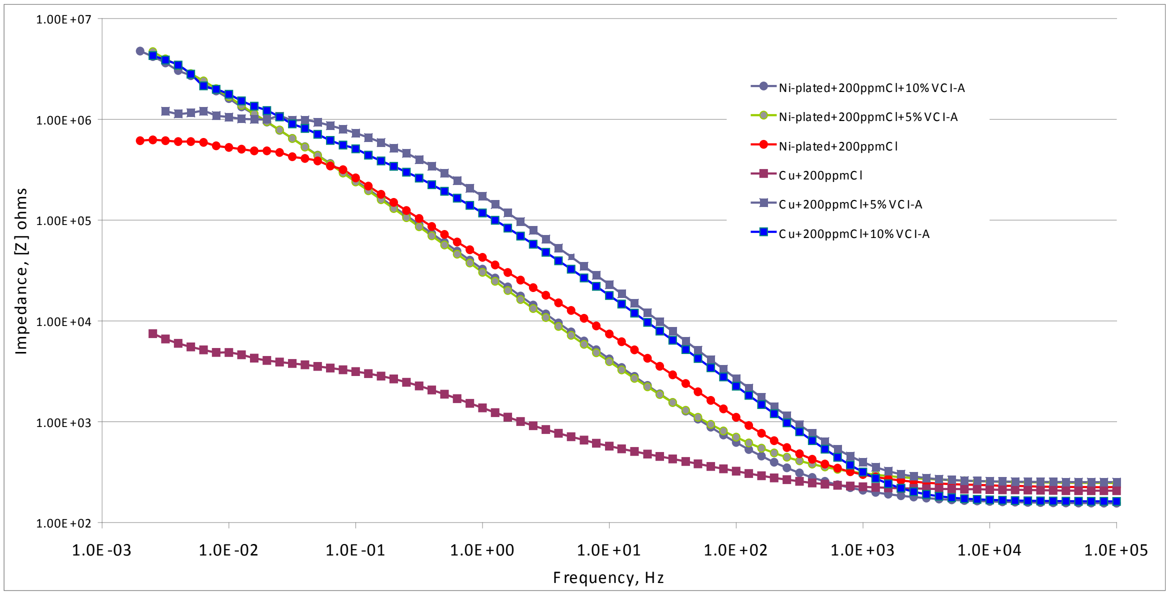

Figure 4: Electrochemical impedance spectroscopy Bode plots for Cu and Ni-plated Cu in different Inhibitor-A concentrations.

Stress Corrosion Cracking

Susceptibility to SCC was determined for these alloys using ASTM G38 C-ring samples (ASTM G38) [9] at an applied stress of 60% to 90% of their yield strength using ASTM G44 alternate immersion technique. None of the alloys showed any susceptibility to SCC in different concentrations of inhibitor. The only sample that showed crack initiation was brass C36000 at 90% applied stress level in the salt solution. However, when the inhibitor was added, no sign of any cracking was found. Figure 5 shows fracture surfaces for the C36000 C-ring samples after 200 cycles in ASTM G44. Figure 5 demonstrates the ductile dimple-type overload failure morphology for the samples tested in corrosive environments (chloride ions) with inhibitor as compared to the intergranular failure surfaces seen for samples with no inhibitor.

Verification of the Inhibition Mechanism

The corrosion inhibition mechanism of Inhibitor-A was investigated using the polarization resistance data acquired from the cyclic polarization and EIS tests. The increased polarization resistance can be attributed to the adsorption of inhibitor molecules to the metal surfaces. The addition of inhibitor has increased the R_p value for all alloys (Tables 1,2). The high R_p value is due to the progressive adsorption of inhibitor molecules and film formation on the metal surface. The data obtained from the electrochemical experiments best fit the Langmuir adsorption isotherm.

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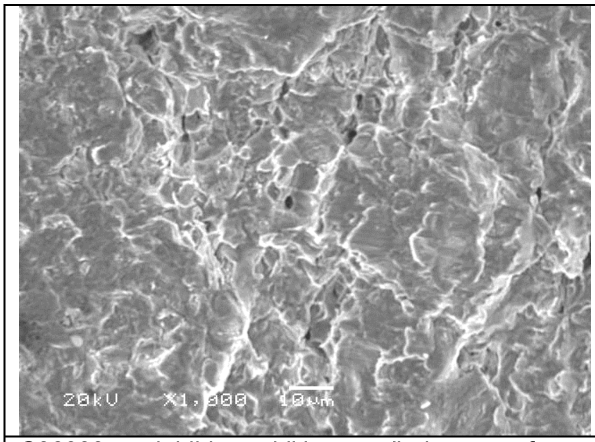
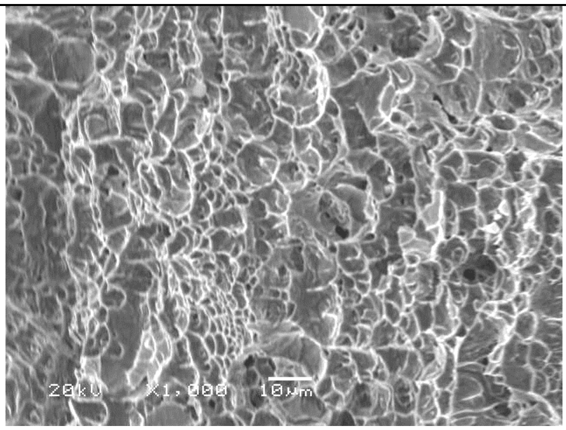
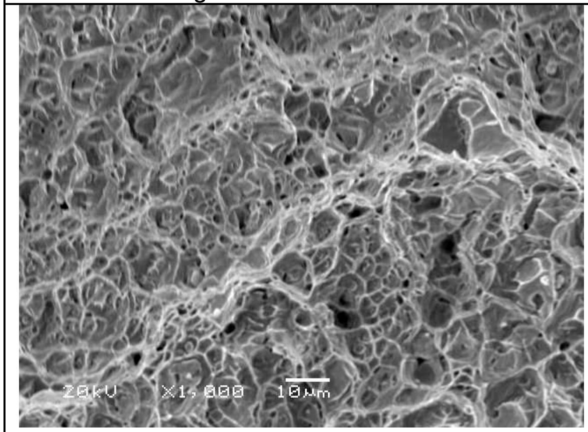
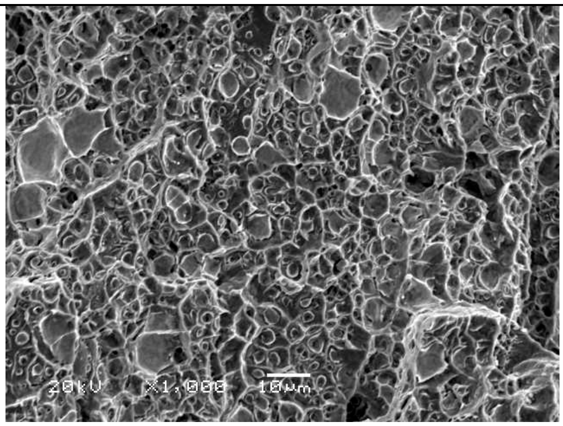
	
C36000, no inhibitor addition, applied stress of 90% Yield strength	C36000, 5% Inhibitor A
	
C36000, 10% Inhibitor A	C69300, 5% Inhibitor A

Figure 5: SEM fractographs of the fracture surface for C-ring samples of C36000 and C69300 alloys **after SCC tests in different solutions.**

The important thermodynamic values (changes in enthalpy of adsorption and changes in free standard energy of adsorption) were obtained with adsorption isotherms and classical thermodynamics. The value of ΔG_{ad} could be used to identify the adsorption mechanism.[6] In chemical adsorption, ΔG_{ad} is usually much higher than physical adsorption. The criterion for chemical adsorption varies depending on the paper referenced;[4] the range is stated to be between -40 kJ/mol and -100 kJ/mol energy. Physical adsorption requires energy between -5 to -20 kJ/mol.[4] The analysis of Inhibitor-A showed the enthalpy of adsorption to be roughly -10 to -14 kJ/mol (Figure 6); this would indicate that the inhibitor has strong physical adsorption to the metal surface. The majority of corrosion damage to turbo-machinery systems, however, occurs during the shutdown period due to chemistry changes and stagnant conditions in localized areas. Therefore, a corrosion inhibitor with strong physical adsorption to the metal surface is preferred.

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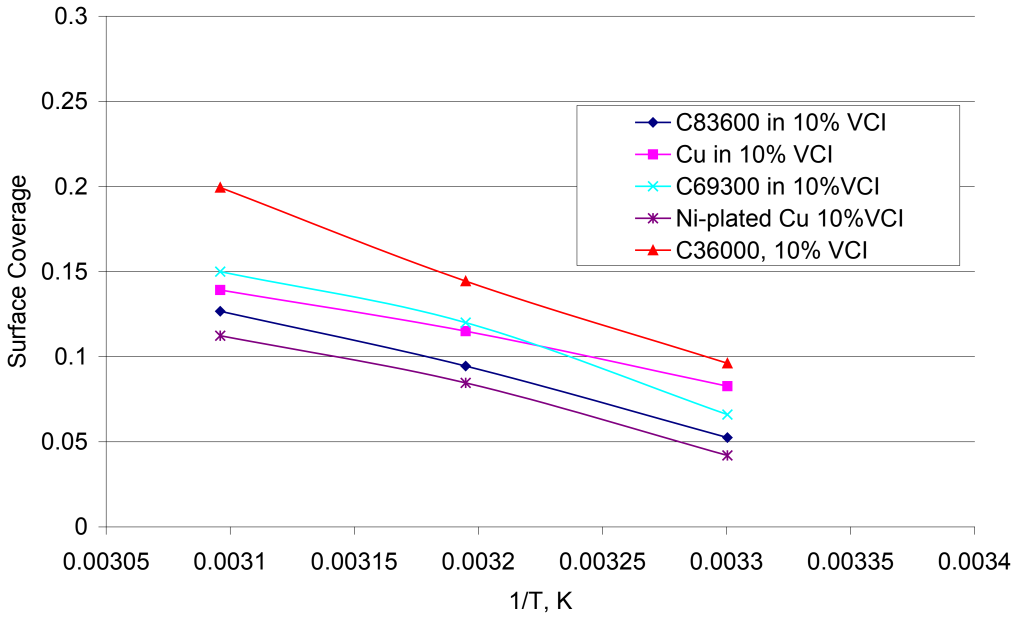

Figure 6: Langmuir adsorption isotherm showing the relationship between fractional **surface coverage by Inhibitor-A and** and inverse of **temperature for different alloys.**

CONCLUSIONS

Corrosion behavior of turbo-machinery system auxiliary component alloys in the presence of a vapor corrosion inhibitor was investigated. Electrochemical impedance spectroscopy and cyclic polarization in room temperature and elevated temperature showed no adverse effects on any alloys; in fact in most cases corrosion was inhibited. Cyclic polarization behavior for samples in the vapor inhibitors showed a significant positive shift in the passive film breakdown potential for copper alloys. The increase in the passive film range will improve localized corrosion resistance.

The data acquired from electrochemical tests showed that inhibitor adsorption to these alloy surfaces fits with the Langmuir adsorption isotherm; the enthalpy of adsorption is approximately -10 to -12 for Cu-alloys and about -14 to -16 (for Ni-plated) kJ/mol which suggests this inhibitor function is based on a physisorption mechanism.

The tests showed less SCC susceptibility in environments with Inhibitor-A for all alloys including active alloy such as C36000. Almost no crack initiation was observed for the alloys tested in the chloride solution with 10% Inhibitor-A. In the absence of inhibitor only C36000 showed crack initiation when the applied stress was 90% of its yield strength.

In summary, Inhibitor-A can be deduced to provide effective corrosion protection for steel, copper alloys, nickel-plated parts and all other auxiliary components used in low pressure steam turbines during the shutdown period.

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