

RESEARCH ON MULTIPURPOSE CORROSION INHIBITORS FOR AEROSPACE MATERIALS IN NAVAL ENVIRONMENTS

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A study to formulate corrosion inhibitor systems for the control of common aircraft corrosion and corrosion assisted failures has been conducted. The mechanisms of principal driving corrosion processes and control are considered to devise new multipurpose inhibitor systems which can protect high-strength structural alloys from catastrophic failures such as stress corrosion cracking, corrosion fatigue, hydrogen embrittlement, exfoliation and wear.

BACKGROUND

Corrosion damages in Naval aircraft range from simple general corrosion to complete failure of structural parts much below their design strength level. According to new estimates (NBS and 3M data) the Navy spends nearly \$450 million dollars annually in corrosion costs on aircraft alone. Based on failure reports from the fleet, the major corrosion damages appear in the form of structural breakdown such as exfoliation, stress corrosion cracking, corrosion fatigue or hydrogen embrittlement. They mostly originate from pitting and/or crevice corrosion type of attack. These are generally caused by imperfections in the structure or porosity and breakdown in the protective films and coatings. Since paints and finishes used for this purpose are only temporary barriers to the environment, they are likely to break down easily and provide active centers for more accelerated attack of the underlying metal. Thus, the presence of a corrosion inhibitor in the system is essential to provide corrosion protection to the underlying metal.

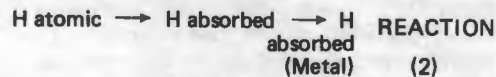
In an earlier study¹ it was determined that the mechanisms involved in various corrosion failures have some basic common factors as the governing rules of the process. Principally they are classified as follows:

1. Agarwala, V.S., "Accelerated Environmental Testing of Aerospace Materials for the Study of Stress Corrosion Cracking and Hydrogen Embrittlement," Oct 1977, NRC Senior Associateship Report, Nat. Acad. Sci., Washington, DC.

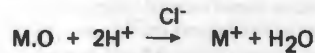
1. Anodic dissolution of metal



2. Cathodic reduction of hydrogen



3. Breakdown of passivity (auto catalytic)



4. Plastic deformation (mechanical and metallurgical)

Emergence of Slip Steps \rightarrow New Active Surfaces

Thus, reactions 1 and 2 proceed. Here the symbols have their usual meaning and M stands for any metal such as iron.

Among these reactions, reaction 2 is probably the most critical in causing structural damages. Since all of the above reactions are of an electrochemical nature, they can be mechanically controlled by chemicals; i.e., by utilizing the selective reduction-oxidation (redox) properties of certain inorganic compounds. Currently a number of inorganic compounds are known which can be classified as corrosion inhibitors. They mostly

control either anodic or cathodic reactions. However, as corrosion failures result from a combination of several of the above reactions, a single inorganic compound will be unable to perform a multifunctional task. Thus, a combination of several different redox systems is most essential for the effective control of corrosion and corrosion assisted failures.

OBJECTIVES

To analyze the mechanisms of corrosion and corrosion assisted failures with a view to devising new multipurpose versatile inhibitors or inhibitor systems which can protect high-strength structural alloys from catastrophic failures such as stress corrosion cracking, corrosion fatigue, hydrogen or environmental embrittlement, exfoliation and wear. It is also anticipated that this research will provide meaningful data, test results and methods which may be used to produce a product or procedure that can be of immediate use to naval aircraft.

PROGRESS

Selection and determinations of inorganic compounds as functional corrosion inhibitors and their formulation into one versatile inhibitor system are the key elements of this program. A rapid electrochemical technique was, therefore, required to perform the screening and selection process. Earlier² a technique was developed by which inorganic compounds could be linked with a quaternary ammonium salt by an anion exchange reaction, which makes them soluble in many organic solvents. Use of this method, thus, reduces the difficulty of retaining the redox functional properties of the additives compounded in the formulation (mixture) without encountering interference. In another program³, it was also established that inorganic compounds dissolved in organic solvents were much more efficient and long lasting as inhibitors than their counterpart in aqueous phase.

2. *Ohr, J., and Clark, K.G., "The Chemistry and Application for the Solubilization of Chromate Salts in Non-Polar Organic Solvents," NAVAIRDEVCON Report No. NADC-78017-60.*

3. *DeLuccia, J.J., and Agarwala, V.S., "Research on Catastrophic Damage Phenomena and Damage Control in Naval Aircraft Alloys," IR Work Unit No. GC153, 1978 IR/IED Annual Report.*

The electrochemical method developed for inhibitor selection was a galvanic corrosion monitor probe as shown in figure 1. The probe works on the principles of a galvanic cell and is comprised of a series of plates of two different metals (steel and copper) sandwiched together alternately separated by an electrical insulator and encapsulated in epoxy. An electronic zero-resistance ammeter circuit connects them externally while the edges of the plates are ground, polished, and exposed to the environment. The environmental condensation on these plates forms a thin film of electrolyte which completes the galvanic circuit. The galvanic output of this cell becomes a measure of the corrosivity of the condensed film

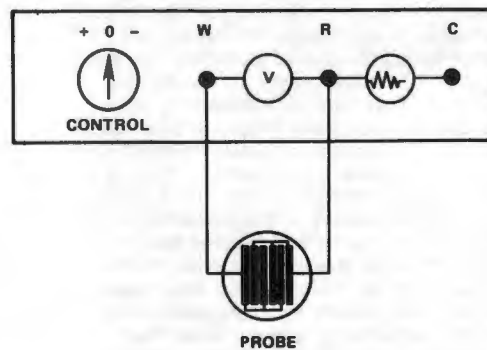


FIGURE 1 - INSTRUMENTATION FOR CORROSION MONITOR PROBE

(or environment). The outdoor (e.g., aircraft carrier) and indoor (in simulated environmental chamber) testing of this probe has been successful in measuring the severity of the naval environment. This technique was used to evaluate potential corrosion inhibitors. However, in these evaluations the probe was half submerged into the test solutions containing the inhibitor and the salt etc. A plot of corrosion monitor probe output versus time under some test conditions is shown in figure 2. The results illustrate a direct correlation between the monitor output and the corrosion and/or inhibitive properties of the test media. Using this technique a large number of compounds are evaluated as potential anodic (or passivating type) inhibitors. Chemicals like dichromates, nitrites, osmiates, permanganates, etc. fall in this category.

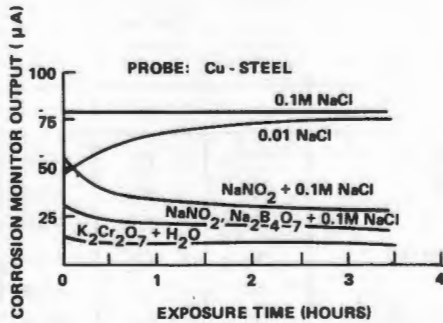


FIGURE 2 - EVALUATION OF CANDIDATE INHIBITORS USING A CORROSION MONITOR PROBE (STEEL/COPPER)

In order to evaluate cathodic type inhibitors; i.e., those which control the hydrogen evolution reaction, an electrochemical hydrogen permeation technique was used. The details of the method are described elsewhere⁴. However, in these investigations the electrolyte in the input chamber (i.e., where H is evolved cathodically) was added with the test inhibitors to determine their effects on the hydrogen evolution reaction and/or hydrogen entry into the metal (Armco iron). The results of such a measurement are illus-

trated in figure 3. Among the compounds tested the dichromate, palladate and lanthanum nitrate have produced a very significant decrease in H permeation rate from that of the control without an inhibitor. The dichromate has shown the maximum cathodic inhibition as the rate of H diffused through the metal was lowered by almost 50%. Several other potential candidate inhibitors are also being evaluated currently. Based on the above knowledge and the experience gained from the earlier work³ a few formulations have been made and evaluated. Adogen 464, known chemically as methyl trialkyl (C₈-C₁₀) ammonium chloride, was used as a phase transfer catalyst to dissolve the inorganic compounds in mineral spirits. The tests were performed to investigate the effects of some of the combination inhibitors on low-cycle fatigue life of AISI 4340 steel (260-280 ksi) when exposed to high humidity and chloride containing environments. The details of

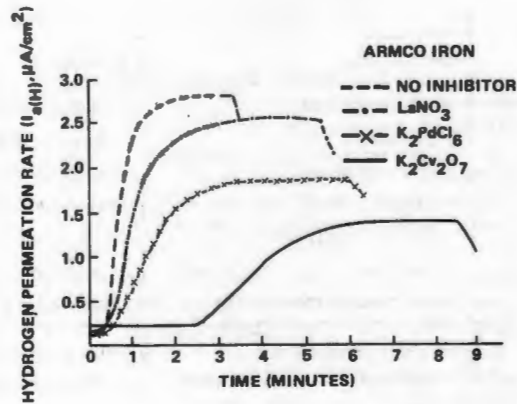


FIGURE 3 - EFFECTS OF INHIBITORS ON HYDROGEN PERMEATION IN IRON

4. Agarwala, V.S., and DeLuccia, J.J., "Effects of a Magnetic Field on Hydrogen Evolution Reaction and Its Diffusion in Armco Iron," Proceedings of 7th International Congress on Metallic Corrosion, 1978, Rio de Janeiro, Brazil.

these tests are described elsewhere⁵. A summary of the data obtained is given in table I. As shown in table I, the results clearly demonstrate that the concept of combining several functional inhibitors into one system was very effective in retarding crack growth rate. In particular, a combination inhibitor system containing dichromate, nitrite and borate compounds (c.f. table I) showed an excellent fatigue life for 4340 steel compared to the results shown by their individual components. However, when chloride was also added to the environment, the effect of inhibition disappeared until molybdate was added. This is because molybdate has been known to counteract the effect of chloride by influencing the kinetics of repassivation.

The effect of these inhibitors was also studied on a high strength 7075-T6 aluminum alloy for their stress corrosion cracking (SCC) inhibition properties. For this evaluation, double cantilever beam (DCB) specimens were used and pop-in cracked under a constant load applied by two bolts. The technique used was developed by Hyatt⁶ for determining SCC resistance of aluminum alloys. Because of the simplicity of this method a number of test specimens can be tested at the same time. The test chamber in these tests was kept at room temperature and a high relative humidity (>95%) was maintained at all times. Addition of inhibitors and salt solution (3.5% NaCl) into the notch area of the specimen was done by putting a drop of these liquids through a very thin wick of cotton inserted in the notch.

	INHIBITORS APPLIED TO NOTCH AREA	MECHANISMS INVOLVED	CRACK GROWTH RATE MICRO-IN./CYCLE	STRESS INTENSITY FACTOR ΔK , KSI $\sqrt{\text{IN.}}$	FATIGUE LIFE, CYCLES
	DRY AIR ONLY	NO CORROSION	12	70	17,000
↑ MOIST AIR ONLY ↓	NO INHIBITOR USED	SEVERE CORROSION AND H. E.	110	33	1,800
	DICHROMATE	PASSIVE FILM FORMATION	42	52	6,800
	NITRITE + BORATE	MOSTLY pH ADJUSTMENT	65	35	3,300
	HEXAPALLADATE	ACCELERATE H RECOMBINATION	45	> 40	4,000
	LANTHANUM NITRATE	H GETTERING ACTION	50	> 40	4,800
	DICHROMATE + NITRITE + BORATE	PASSIVATION AND pH ADJUSTMENT	27	55	9,000
	CERATE + NITRITE + BORATE	PASSIVATION AND pH ADJUSTMENT	38	45	6,400
↑ MOIST AIR + CHLORIDE ↓	NO INHIBITOR USED	SEVERE CORROSION AND SEVERE H.E.	150	32	1,200
	DICHROMATE + NITRITE + BORATE	NO PASSIVATION, SEVERE H. E.	200	34	1,200
	MOLYBDATE	SOME PASSIVATION AGAINST CHLORIDE	61	46	4,500
	DICHROMATE + NITRITE + BORATE + MOLYBDATE	PASSIVATION, pH ADJUSTMENT AND CHLORIDE RESISTANCE	28	48	6,500

TABLE I - EFFECT OF FUNCTIONAL PROPERTIES OF VARIOUS CRACK ARRESTMENT INHIBITORS ON LOW-CYCLE FATIGUE OF HIGH STRENGTH 4340 STEEL

5. Agarwala, V.S., and DeLuccia, J.J., "New Inhibitors of Crack Arrestment in Corrosion Fatigue of High-Strength Steels," *Corrosion*, 36(4), pp. 208-212, 1980.

6. Hyatt, M.V., "Use of Pre-cracked Specimens in Selecting Heat Treatments for Stress Corrosion Resistance in High Strength Al Alloys," *Corrosion*, Vol. 26 No. 11, pp. 487-503, 1970.

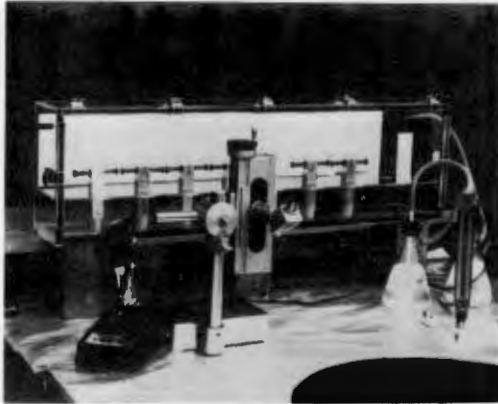


FIGURE 4 - ENVIRONMENTAL TEST CHAMBER CONTAINING DCB SPECIMENS FOR DETERMINING SCC OF 7075-T6 AL ALLOYS

Only a drop of the test solutions were added once a week. The crack growth of the specimen was monitored periodically. The results obtained from this test are shown in figure 5 as crack growth rate versus stress intensity factor (da/dt versus K_I) curves for an inhibitor combination of dichromate + nitrite + borate + molybdate (DNBM), in two environmental conditions. A marked crack growth retardation effect was observed for DNBM as demonstrated by the shift in the da/dt versus K_I curves to a much higher stress intensity value. In other words, the K_{ISCC} Value For 7075-T6 aluminum alloy was increased by a factor of two when these inhibitors were used. Efforts are continuing to evaluate several other inhibitors.

FUTURE PLANNING

Electrochemical investigation of selected candidate corrosion inhibitors will be continued to study their anodic and cathodic (hydrogen permeation) effects. Several other formulations will be made in other possible alternate non aqueous media to seek greater stability of the compounds present. Evaluation of the inhibitors will be continued and extended to other forms of corrosion such as exfoliation and wear.

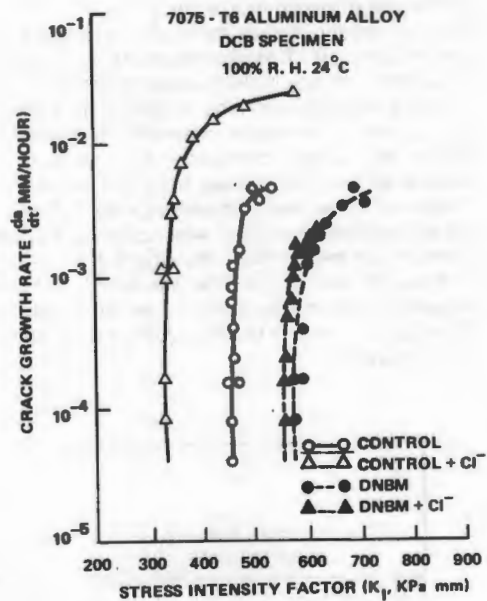


FIGURE 5 - EFFECT OF INHIBITORS ON STRESS CORROSION CRACKING PROPERTIES OF 7075-T6 ALUMINUM ALLOY

The research as planned is expected to translate into useful products, procedures and techniques for fleet application. Progress has already been made in the development of the corrosion monitor probe and a formulation for inhibiting corrosion fatigue in high-strength steels.