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Alloy Compatibility with Several Cleaning Agents

Prepared by D. L. DULL, L. RAYMOND, and R. J. USELL
Materials Sciences Laboratory

69 MAY 29

Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. F04701-68-C-0200.

This report, which documents research carried out from 1 September 1968 to 31 January 1969, was submitted on 29 April to Lieutenant Jerry J. Smith, SMTTM, for review and approval.

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Approved

W C Riley

W. C. Riley, Director
Materials Sciences Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Jerry J Smith

Jerry J. Smith
2nd Lt., United States Air Force
Project Officer

ABSTRACT

Cleaning agents have been implicated in several aerospace structural system failures due to stress corrosion; however, the exact sources of the problems have not been established. This investigation was conducted to screen the compatibility of four common aerospace structural materials with three common cleaning agent environments in order to identify the problem sources and suggest methods to avoid these problems. It is indicated that the potentially most deleterious effect is due to a corrosion product containing chlorine that may degrade the protective film and expose fresh metal to the service environment.

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I. INTRODUCTION

Cleaning agents have been implicated in several stress corrosion failures experienced on the Titan program; however, causality has not been established. For example, results of an investigation of leakage in the stage II oxidizer feed line bellows of missile B-66 indicate that the stress corrosion failure of the type 321 stainless steel bellows was caused by chloride entrapment (Ref. 1). These results also indicate that the chloride was present in the trichloroethylene cleaning agent and/or rinse water. Stress corrosion failure was recently noted in a type 347 stainless steel pressure switch diaphram of a Titan III Transtage helium pressurization system at Martin Company, Denver.[1] This failure was believed to result from trichloroethylene entrapment in a dead-end fluid cavity during a cleaning operation. Contamination and/or corrosion have been observed in several other propellant systems (of other companies) where trichloroethylene had been used on aluminum and stainless steel surfaces as the final cleaning agent.

Despite their protective oxide film, titanium alloys have been subjected to stress corrosion in several halogenated hydrocarbons (Refs. 2-4). The available data, although not always well documented, led Bowman to postulate a mechanism wherein chlorine present in the nonaqueous environments was responsible for the attack (Refs. 5, 6).

This investigation was conducted to screen the compatibility of four common aerospace structural materials with three common cleaning agents. The general and stress corrosion behavior of type 347 stainless steel, AM-350 steel, Ti-6Al,4V, and 7075-T6 aluminum alloy was investigated at room temperature in trichloroethylene, a mixture of trichloroethylene plus water, and methyl ethyl ketone environments.

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[1] S. Lewis, Stress Corrosion of Pressure Switch After Exposure to Trichloroethylene, IOC 68-2150.20.4.1-13, The Aerospace Corporation, El Segundo, Calif.(10 July 1963).

II. BACKGROUND

The information necessary to characterize the compatibility of an environment with a given material is usually obtained from three distinct tests that can be performed sequentially. The simplest of the three is the test to provide information on general corrosion, referent from weight-loss tests of small coupons. This test also provides information on the contamination of the environment by the corrosion products. In the second test, stressed-smooth specimens are used and information similar to that of the weight-loss test is obtained, in addition to the effect of stress on material compatibility. Intentionally flawed stressed specimens are used in the third test, which reflects the fracture mechanics philosophy that fabrication and inspection techniques are fallible, and, therefore, the tendency for the environment to cause flaw growth should be investigated. This test is particularly important, since it is possible for a material/environment system to result in flaw growth when it does not produce general corrosion. Thus, a material/environment combination could satisfy the first two tests, and yet the material and environment could be incompatible due to flaw growth.

It is believed that the information on cleaning agent compatibility of interest in aerospace systems can be obtained from two types of specimens: (1) unstressed specimens indicate the nature of general corrosion (e.g., uniform attack, pitting) and the nature of the corrosion products; the nature of the corrosion products may be important in flow situations (e.g., valves, bellows) where clogging is possible; and (2) stressed precracked specimens indicate the likelihood of flaw growth to leak or burst in pressurized systems. Also, qualitative information concerning the effect of stress on the corrosion can be obtained by noting variations of attack in the various stressed regions of the specimens. Along the crack line the stresses are low; near the crack tip they approach the yield strength; away from the crack they are intermediate, and range from 50 to 75 percent of the yield strength.

Fracture mechanics provides the framework for describing the crack-bearing properties of a metal in the presence of an environment (Refs. 7-9). First, the critical stress intensity parameter K_c is determined in an innocuous environment. Second, a series of precracked specimens is exposed to the environment while loaded, such that the applied stress intensities are fractions of K_c and the time-to-failure can be noted. In general, there will be a threshold stress intensity level K_{th} below which no significant flaw growth will occur. The ratio K_{th} to K_c is a measure of the degree of degradation associated with the environment and is the parameter of interest in this phase of the investigation.

III. MATERIALS

Triplicate tensile specimens were tested in a 20,000-lb-capacity Instron testing machine to determine the mechanical properties of the materials. The ultimate strength, yield strength, and percent elongation in a 2-in.-gage length are shown in Table 1.

It should be noted that with the thicknesses of materials used in this investigation plane stress fracture resulted, and the values obtained were dependant on specimen geometry. Since relative values were determined (i.e., K_{th} and K_c both measured with the same specimen geometry), the use of these specimens was justified. In addition, the thicknesses of materials used compared favorably with those used in many aerospace applications.

Trichlorethylene and methyl ethyl ketone were the cleaning agents used in this investigation; typical chemical analyses of these agents are shown in Table 2.

Table 1. Results of Mechanical Properties and Fracture Toughness Testing

Material	Yield Strength, ksi	Ultimate Tensile Strength, ksi	Percent Elongation in 2-in.-Gage Length	Nominal Thickness, in.	Fracture Toughness K_c air, ksi$\sqrt{\text{in.}}$
347 stainless steel	46	94	44	0.061	66[a]
Ti-6Al-4V	159	170	8	0.048	88
7075-T6 aluminum alloy	75	81	12	0.091	48
AM-350 steel	157	196	20[b]	0.048	155

[a] $\sigma_{net}/\sigma_{YS} > 1$

[b] Percent elongation in 1-in.-gage length

Table 2. Chemical Analysis of Trichloroethylene and Methyl Ethyl Ketone

Trichloroethylene ($CHCl:CCl_2$)	
Residue after evaporation, %	0.001
Acidity (as HCl), %	0.0005
Alkalinity (as NaOH), %	0.001
Heavy metals (as Pb), %	0.0001
Maximum solubility of water	690 ppm

Methyl Ethyl Ketone ($CH_3COC_2H_5$)	
Minimum content methyl ethyl ketone, %	99 min
Acidity (as HAc), %	0.003 max
Nonvolative matter, %	0.002 max per 100 ml

IV. EXPERIMENTAL PROCEDURE AND RESULTS

A. EXPERIMENTAL

Single-edge notched (SEN) specimens were increasingly loaded in a 20,000-lb-capacity Instron testing machine, until the crack became unstable and extended abruptly, to determine the fracture toughness K_c in air. No slow crack growth was observed, except in the 347 stainless steel specimen. Measurements of crack opening displacement, using a double-cantilever compliance gauge, indicated no evidence of pop-in. Maximum loads were used to calculate fracture toughness. The boundary collocation K calibration of the SEN specimen (Ref. 10) was used to convert the measured parameters (load, crack length, and specimen geometry) to K_c values.

Duplicate 1-in.-square specimens were sanded with No. 320 grit metallographic paper and immersed in the environments for periods up to four months. The test plan required the use of polyethylene bottles to contain the environments around the stressed specimens. Unstressed coupons were immersed in environments contained in both polyethylene bottles and glass flasks to determine if polyethylene provided a neutral container. No differences in corrosion rates were noted on visual observation of corrosion product formation. Analysis was performed of corrosion products by x-ray fluorescence and diffraction techniques.

Specimens 1 × 8-in. × sheet thickness, with the long dimension in the rolling direction, were obtained. The specimens were sanded with No. 320 grit metallographic paper, edge-notched to a depth of 0.15 in., and fatigue precracked to a depth of from 0.25 to 0.40 in. using a modified Manlabs, Inc. Charpy Impact specimen fatigue precracker. The cleaning agents were supported around the specimens in pint-sized polyethylene bottles with slits cut on opposite sides so that the specimens could be inserted to enclose the precracked area. The bottles were then sealed with either General Electric Silicone RTV-102 or RTV-156 and loaded in 12,000-lb-capacity Satec creep testing machines to applied stress intensities lower than the previously determined K_c values for air. The K_c data obtained in air contained scatter of about ±8 percent, therefore, the highest K_c value used was limited to 0.85 K_c to eliminate failures due to specimen/test procedure variations.

B. RESULTS

1. TYPE 347 STAINLESS STEEL

The concepts of fracture mechanics are usually applied to describe fracture when net stresses are less than the yield strength of the subject material. When failure stresses are near the yield strength, a notch strength approach can be used. It was found that in a range of widths convenient for this investigation, net stresses at failure were always more than the yield strength of 347 stainless steel. The effect of specimen width on both K_c and σ_{net}/σ_{YS} is shown in Figs. 1 and 2, respectively. Since there was no reason for preference of one method of describing failure over another, and since the specimens used here were geometrically similar to the other specimens used in this work, the K_c description of failures was retained.

No crack growth was observed in specimens loaded to stress intensities greater than 0.85 K_c for more than 800 hr in trichloroethylene. General corrosion and some pitting that were not a function of stress level occurred within 200 to 400 hr. The corrosion product obtained from unstressed coupons was a reddish-brown color, granular in form. Analysis by x-ray fluorescence revealed that the product contained chlorine, chromium, iron and nickel; the diffraction pattern was that of a complex oxide.

No crack growth was observed in specimens loaded to stress intensities greater than 0.85 K_c for more than 1000 hr in trichloroethylene plus water. A slight discoloration, interpreted to be an oxide film, formed after a few hundred hours, and some pitting occurred in unstressed coupons exposed for more than five months.

No crack growth was observed in specimens loaded to stress intensities greater than 0.85 K_c for more than 1000 hr in methyl ethyl ketone; nor was general corrosion observed after 1000 hr.

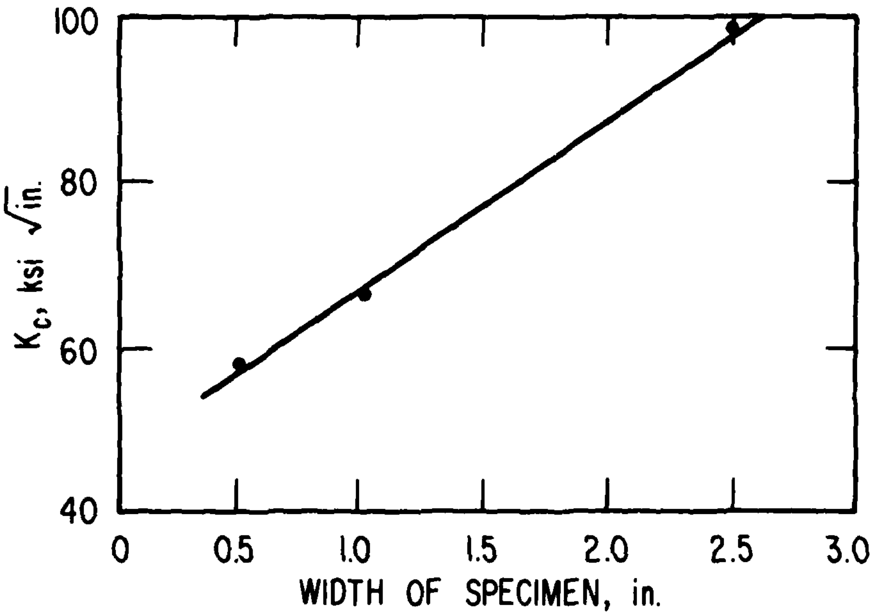

Figure 1. Fracture Toughness Versus SEN Specimen Width for 347 Stainless Steel

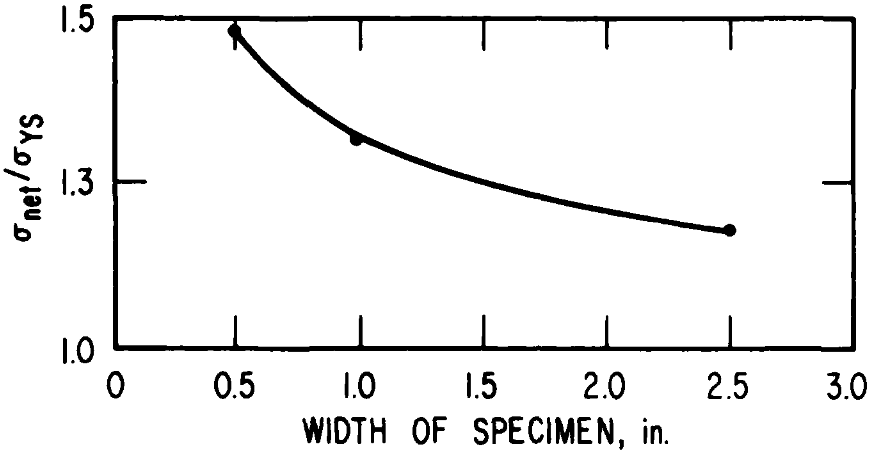

Figure 2. Net Strength/Yield Strength Versus SEN Specimen Width for 347 Stainless Steel

2. AM-350

Definite evidence of crack growth was observed in specimens loaded to stress intensities greater than 0.72 K_c in both trichloroethylene and trichloroethylene plus water. See Fig. 3. The closed data points of this figure represent specimens that did not crack but were unloaded at the times indicated; the open data points indicate fracture. Both trichloroethylene environments produced a green-colored adherent corrosion product that could be flaked from the metal surface. The corrosion product contained iron, chromium, and chlorine, and was identified as a complex iron-chromium oxide.

No crack growth was observed in specimens loaded to stress intensities greater than 0.80 K_c in methyl ethyl ketone for over 1000 hr, nor was a corrosion product formed.

3. Ti-6Al-4V

No crack growth due to any of the cleaning agent environments was observed in these specimens loaded to 0.85 K_c; however, general corrosion was observed in unstressed coupons within 3000 hr in only the trichloroethylene environment. Analysis of the corrosion residue by x-ray fluorescence and diffraction techniques revealed it to be an amorphous titanium and chlorine mixture.

4. 7075-T6 ALUMINUM ALLOY

No crack growth was observed in these specimens loaded to 0.85 K_c in trichloroethylene for more than 500 hr; however, general corrosion occurred within 200 hr. The corrosion was not a function of stress, and the residue was determined to be an amorphous aluminum and chlorine mixture.

Trichloroethylene plus water caused failure in the 7075-T6 aluminum alloy specimens due to a reduction in cross section. Corrosion products formed within 24 hr, and were determined to be an amorphous aluminum and chlorine mixture.

No crack growth was observed in specimens loaded to 0.85 K_c in methyl ethyl ketone for 1000 hr, nor was general corrosion noted.

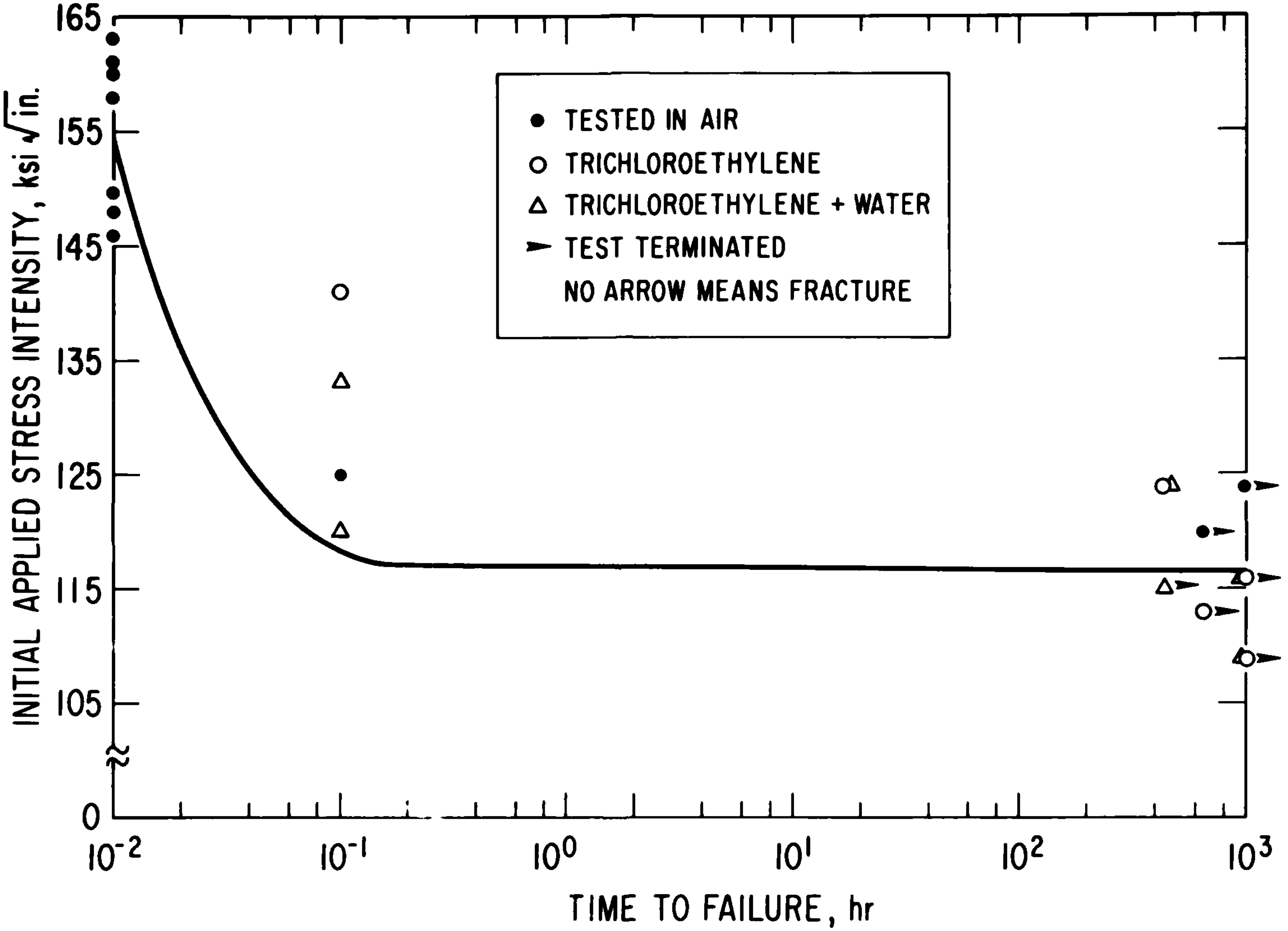

Figure 3. AM-350 Exposed to Trichloroethylene and Trichloroethylene plus Water

V. DISCUSSION OF RESULTS

A. STRUCTURAL FAILURES

1. DIRECT

Two of the systems tested indicated the possibility of component structural failure due to direct interaction of the cleaning agent and the material. AM-350 steel immersed in trichloroethylene environment yielded K_{th} to K_c of 0.72; corrosion of 7075-T6 aluminum was very rapid in trichloroethylene plus water. Trichloroethylene should not cause any damage to a component during cleaning since, without residual stresses, the stress intensities are likely to be low; however, it could cause some damage if used as the hydraulic medium during proof testing.

2. INDIRECT

It is believed that the most insidious aspect of material/cleaning agent interaction observed in this investigation was the occurrence of chlorine in the corrosion products. It was found, in at least one case, that the chief role of chlorine in an environmentally induced flaw-growth situation was to aid the degradation of the oxide coating on a passivating material (Ref. 4). In that case, the Ti-6Al-4V alloy was loaded both before and after exposure to either Freon MF or Freon MF plus chlorine; the results are shown in Figs. 4 and 5. Figure 4 shows that loading prior to exposure to Freon MF permits reformation of the protective oxide coating at the crack tip; loading in the presence of Freon MF does not allow passivation at the crack tip, and attack begins rapidly for all applied stress intensities above the threshold 52 Ksi$\sqrt{\text{in}}$. Figure 5 shows that the oxide coating that forms at the crack tip during the preload in air was slowly degraded by the presence of chlorine in the Freon MF. The fact that the threshold stress intensity was unaffected by the chlorine additions indicates that chlorine plays no active part in the fracture mechanism. The above results indicate that the presence of a residue containing chlorine is a potential source of problems, as illustrated by the following example.

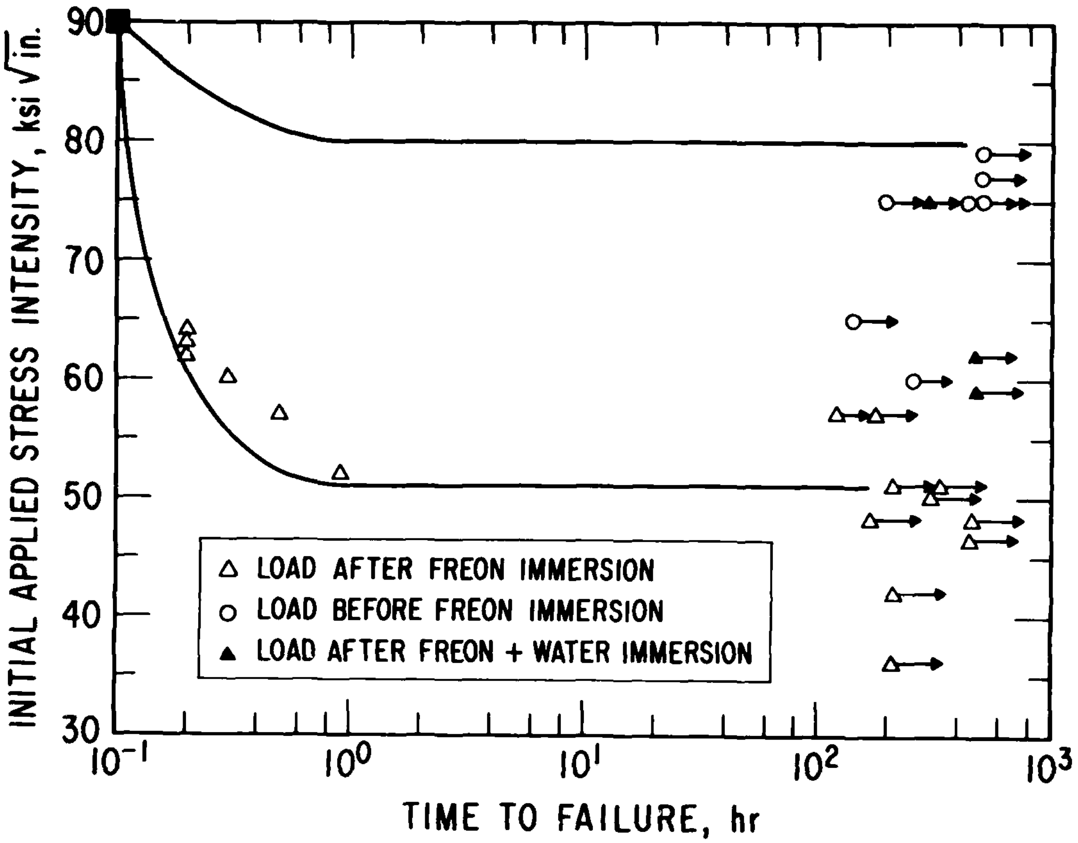

Figure 4. Ti-6Al-4V Exposed to Freon MF

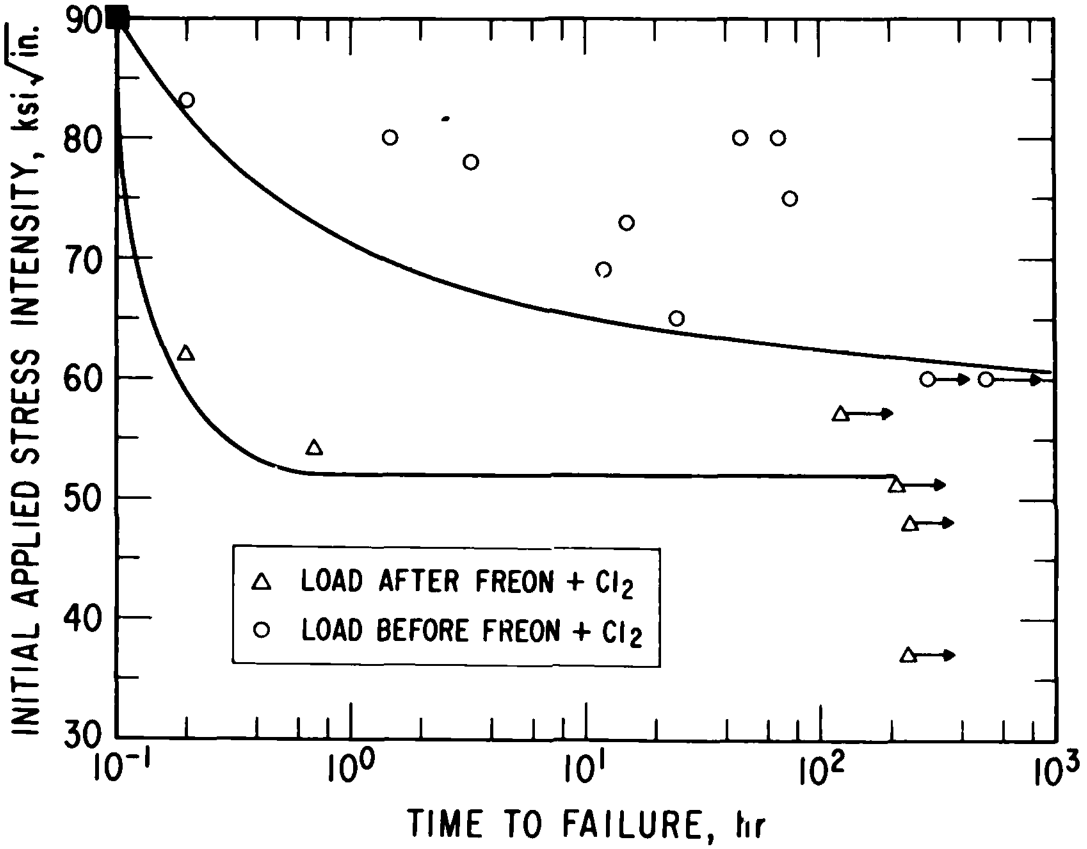

Figure 5. Ti-6Al-4V Exposed to Freon MF $+Cl_2$

First, it is assumed that an adherent residue containing chlorine has formed in the vicinity of or actually in a flaw of a component during the cleaning cycle. This is a likely occurrence, since 50 percent of the systems tested reacted in this manner. Second, it is assumed that the component is composed of a self-passivating material and will contain a pressurized fluid during service. This is also likely, since stainless steel, titanium, and aluminum alloys are common structural materials used in aerospace systems, and since pressurized containers are common aerospace structural configurations. Further, it is assumed that during compatibility testing of the container material and the container fluid, the test specimens were preloaded in air. This is a common test, especially with highly dangerous fluids, such as fuels and oxidizers. Several specimens are self-stressed with load rings or fixtures in open air, then placed in a large common test chamber before application of the fluid environment. The delay between loading and application of the environment could produce results as suggested by the upper curve of Fig. 4; however, if the component retains a residue containing chlorine due to the cleaning agent, the component may react as shown in the upper curve of Fig. 5, resulting in delayed failures. The above example shows the potential problems that may result from improper compatibility testing.

B. NONSTRUCTURAL FAILURES

The general corrosion observed in 50 percent of the systems tested could result in component failure due to clogging of orifices or impairment of intermittently moving parts. It should be noted that the onset of general corrosion in the systems tested was not rapid. With exception of 7075-T6 aluminum alloy in trichloroethylene plus water, none of the systems indicated any corrosion during the first day of exposure; thus, a relatively short cleaning cycle should not cause problems unless substantial entrapment of the cleaning agent is possible.

VI. CONCLUSIONS

This investigation indicates that the passivation process must be considered when studying environmentally induced flaw growth. Specifically, loading of precracked specimens must be done in the presence of the test environment.

General corrosion could result in component failure due to clogging of orifices or impairement of intermittently moving parts.

The potentially most deleterious effect of corrosion is due to a corrosion residue containing chlorine. The chief role of chlorine in an environmentally induced flaw growth situation is to aid the degradation of the oxide coating on a passivating material.

REFERENCES

1. G. R. Curran, Metallurgical Investigation of Leakage in Missile B-66 State II Oxidizer Feed Line Bellows, CR-64-138, Martin Company, Denver Colo.(15 June 1964).
2. W. K. Boyd, Stress Corrosion Cracking of Titanium and Its Alloys, DMIC Memorandum 234, Defense Metals Information Center, Batelle Memorial Institute, Columbus, Ohio(1 April 1968).
3. A. J. Sedriks, P. W. Slattery, E. N. Pugh, Stress Corrosion Cracking of Alpha Titanium in Non-Aqueous Environments, Report 67-7, Rias Div., Martin Company, Baltimore, Md.(June 1967).
4. L. Raymond, R. J. Usell, Flaw Growth in Ti-6Al-4V in Freon Environments, Tr-0200(4250-10)-5, The Aerospace Corporation, El Segundo, Calif. (November 1968).
5. J. Bowman, Accelerated Crack Propagation of Titanium of Methanol, Halogenated Hydrocarbons, and other Solutions, DMIC Memorandum 228, Defense Metals Information Center, Batelle Memorial Institute, Columbus, Ohio(6 March 1967).
6. J. Bowman, Proceedings of AFML Corrosion of Military and Aerospace Equipment Technical Conference, AFML-54-67-329, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio (23 May 1967).
7. J. E. Srawley, W. F. Brown, Jr., Fracture Toughness Testing and its Applications, ASTM STP No. 381, Am. Soc. Testing and Mater., Philadelphia, Pa.(1965).
8. E. A. Steigerwald, "What You Should Know About Fracture Toughness", Metal Progress, Am. Soc. Metals, Metals Park, Ohio(November 1967).
9. W. F. Brown, Jr., J. E. Srawley, Plane Strain Crack Toughness Testing of High Strength Metallic Materials, ASTM STP No. 410, Am. Soc. Testing and Mater., Philadelphia, Pa.(1966).
10. B. Cross, J. E. Srawley, W. F. Brown Jr., Stress Intensity Factors for a Single-Edge Notched Tension Specimen by Boundary Collocation of a Stress Function, NASA TN D-2395, NASA Lewis Research Center, Cleveland, Ohio (August 1964).

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Abstract (Continued)

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