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Flaw Growth in Ti-6Al-4V in Freon Environments

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

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Laboratory Operations
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Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
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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 September 1967 to February 1968, was submitted on 13 January 1969 to Lieutenant Curtis D. Williams, SMTTM, for review and approval.

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.

Curtis D. Williams 2nd Lt USAF

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ABSTRACT

The general and stress corrosion behaviors of Ti-6Al-4V alloy in Freon environments were investigated. Intentionally flawed specimens were examined to determine the ability of the metal to sustain defects on exposure to stress and environment. Freon TF and Freon MF were used as base environments for the study. In addition to testing with commercially pure Freons, chlorine-doped Freons were used. Two thicknesses of solution-treated and aged Ti-6Al-4V alloy were used. The crack-bearing properties of a metal in the presence of an environment is based on the framework of fracture mechanics.

It is indicated that the primary function of stress-intensity in the Ti-6Al-4V/Freon MF interaction is to expose fresh titanium surfaces to the environment through plastic deformation at the crack tip.

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I. INTRODUCTION

Titanium alloys are useful for many aerospace structural applications because of their excellent strength-to-density ratio. Although titanium is one of the more chemically reactive metals, it is useful in many environments because of the protective oxide coating that readily forms on its surface. However, Ti-6Al-4V alloy has not been used with complete success as evidenced by its many failures in nitrogen tetroxide and methanol.[1-6] These stress corrosion failures led Bowman[5,6] to postulate a mechanism wherein chlorine (Cl_2) present in the liquids previously mentioned was responsible for the attack. Bowman further postulated that halogenated hydrocarbons such as Freon TF and Freon MF contain sufficient free Cl_2 to produce stress corrosion failures. This claim was disputed by Bauer.[5]

The general and stress corrosion behaviors of Ti-6Al-4V alloy in Freon environments have been investigated in The Aerospace Corporation's Materials Sciences Laboratory.[7,8] The postulation that commercial Freon TF contains sufficient free Cl_2 to produce stress corrosion cracking in Ti-6Al-4V was invalidated. Neither weld areas or scratched oxide surface layers were adequate to negate this conclusion. This paper describes the study of specimens intentionally flawed to determine the ability of the metal to sustain defects during exposure to stress and environment. Tiffany and Masters found that Freon MF greatly increases the susceptibility to flaw growth of Ti-6Al-4V alloy;[4] the effect of Freon TF on this alloy was much less dramatic. However, neither of the preceding studies attempted to isolate the role of chlorine on the flaw growth behavior, which is the purpose of this paper.

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* Private communication from R. E. Johnson, NASA-MSC, Houston, Texas.

II. BACKGROUND

Fracture mechanics provides the framework for describing the crack-bearing properties of a metal in the presence of an environment.[9-11] 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 so that the applied stress intensities are fractions of K_c and the time-to-failure is noted. In general, there will be a threshold stress intensity level K_{th} below which no significant flaw growth will take place. The ratio K_{th}/K_c is a measure of the degree of degradation associated with the environment and is the parameter of interest in this investigation.

The interest in the K_{th}/K_c ratio can be explained using Fig. 1, which is a plot of the critical applied stress σ_{cr} versus the depth of a long surface flaw, e.g., in a spacecraft pressure vessel, for Ti-6Al-4V.[12] Points on the K_{Ic} curve represent combinations of applied stress and flaw depth which result in rapid fracture. Points on the K_{th} curve represent combinations in the Freon MF environment of σ and a flaw growth too small to produce. Figure 1 shows that using Ti-6Al-4V alloy stressed to 132 ksi results in flaws deeper than 0.024 in., causing fracture of the vessel; flaws deeper than 0.009 in. will eventually increase because of stress corrosion. Thus, the flaw detection limits required to assure reliability are much more stringent when environmentally induced flaw growth is possible. A detailed description of the manner in which K_{th}/K_c information can be used in designing pressure vessels is explained elsewhere.[13]

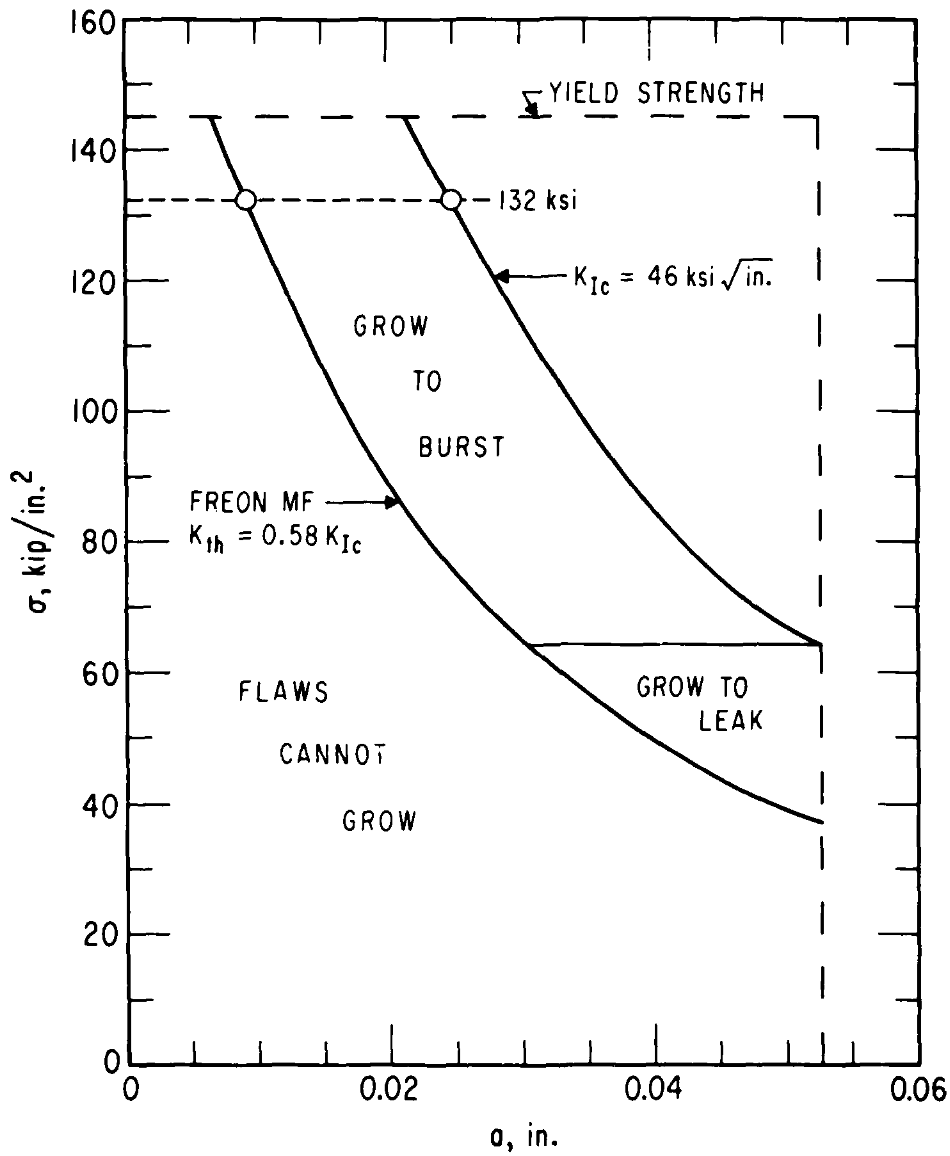

Figure 1. Effect of Environment on Flaw Detection Requirements for Ti-6Al-4V

III. MATERIALS

Two Freons were used as base environments in this study - Freon TF and Freon MF. In addition to testing with commercially pure Freons, chlorine-doped Freons were used. The Freon test liquid was chemically analyzed before and after each test for Cl^-, Cl_2, water, and Ti.[7]

Two thicknesses of solution-treated and aged Ti-6Al-4V alloy were used in this experiment. The chemical analysis and mechanical properties of the metal are listed in Table 1.

Table 1. Chemical Analysis and Mechanical Properties of Ti-6Al-4V

Chemical Composition							
Thickness	C	Fe	N	Al	V	H	O_2
0.048	0.23	0.09	0.014	5.8	4.0	0.007	0.12
0.091	-	-	-	5.5	4.2	-	-

Mechanical Properties			
Thickness	Y.S. ksi	T.S. ksi	Elong. %
0.048	156	168	9
0.091	145	160	13.5*

*1.5-in. gauge length

IV. EXPERIMENTAL PROCEDURE

To determine K_c, single-edge notched (SEN) tensile specimens were increasingly loaded in a 20,000-lb capacity Instron test machine until the crack became unstable and extended abruptly. In this study, no slow crack growth was observed. Measurements of crack opening displacement using a double-cantilevered compliance gauge indicated no evidence of pop-in. Thus, initial crack length and maximum load were the parameters measured. To convert these measured parameters to K_c values, the boundary collocation K (calibration of the SEN tensile specimen due to Gross, et al.[14]) was used.

To determine K_{th}, SEN tensile specimens were loaded in 12,000-lb capacity Satec creep testing machines to levels below K_c, and time-to-failure was noted. K_{th} is the applied K level below which no crack growth is evident. In this experiment, specimens loaded in excess of 200 hr satisfied this definition. The fact that in the commercial Freon environments all failures occurred in less than 1 hr supports this policy. A few specimens were tested to 1000 hr.

Two loading sequences were used. In one sequence, the loading was done while the specimen was immersed in Freon; in the other sequence, the specimen was loaded for several hours in air prior to immersion in Freon. In the former case, the passive oxide coating in the crack-tip region is broken during loading in the presence of the environment, whereas, in the latter case, the passive film was allowed to reform before application of the Freon environment. During the experiment, the cleaning practice described by Kamber, et al.[7] was strictly followed.

To further investigate the effect of contaminants on the behavior of Ti-6Al-4V in Freon, specimens were exposed to water-saturated Freon MF prior to loading because water is the oxidizing agent in Freon. Chemical analyses of the Freon were not performed; however, it is known that Freon MF absorbs about 90 ppm of water at room temperature, whereas the Freon used in the other phases of this study contained from 15 to 25 ppm water.

V. TEST RESULTS

A. FREON MF + Cl_2

Fatigue precracked single-edge notched specimens were used in this phase of the study. These specimens were 0.048-in. thick by 0.98-in. wide and were loaded at a head displacement rate of 0.02 in./min in air. For this material thickness under these conditions, K_c was found to be 90 ksi $\sqrt{in.}$ ± 10%. Load-versus-crack openings were determined for specimens to detect pop-ins. No pop-ins were noted. The load-versus-crack-opening curves resembled typical stress-strain curves for titanium. The deviation from linear behavior occurred at 0.6 ± 0.1 of the maximum load.

For specimens exposed to Freon MF, time-to-failure versus initial applied K_c is plotted in Fig. 2. The data are listed in Tables 2 and 3. The data points with arrows (Fig. 2) indicate that the test was terminated and no crack growth was observed; those without arrows indicate that the specimens failed. The shaded triangles represent the water-saturated Freon MF environment; the circles represent the load before Freon MF immersion.

Figure 2 shows that K_{th}/K_c was 0.57 when specimens were loaded after immersion, increasing to more than 0.85 when specimens were loaded in air for several hours prior to immersion in Freon MF. Figure 2 also shows that loading in the presence of water-saturated Freon MF results in K_{th}/K_c of more than 0.83.

For specimens exposed to Freon MF with from 20 to 100 ppm of Cl_2 added, time-to-failure versus initially applied K_c is plotted in Fig. 3. The data are listed in Tables 2 and 3. Again, the data points with arrows indicate that the test was terminated and no crack growth was observed, while those points without arrows indicate that the specimen failed.

Figure 3 shows that K_{th}/K_c is 0.57 when specimens were loaded after immersion in chlorinated Freon MF. Also, note that the time-to-failure curve is similar to that obtained in the uncontaminated Freon MF environment; i.e., all failures occurred in less than 1 hr.

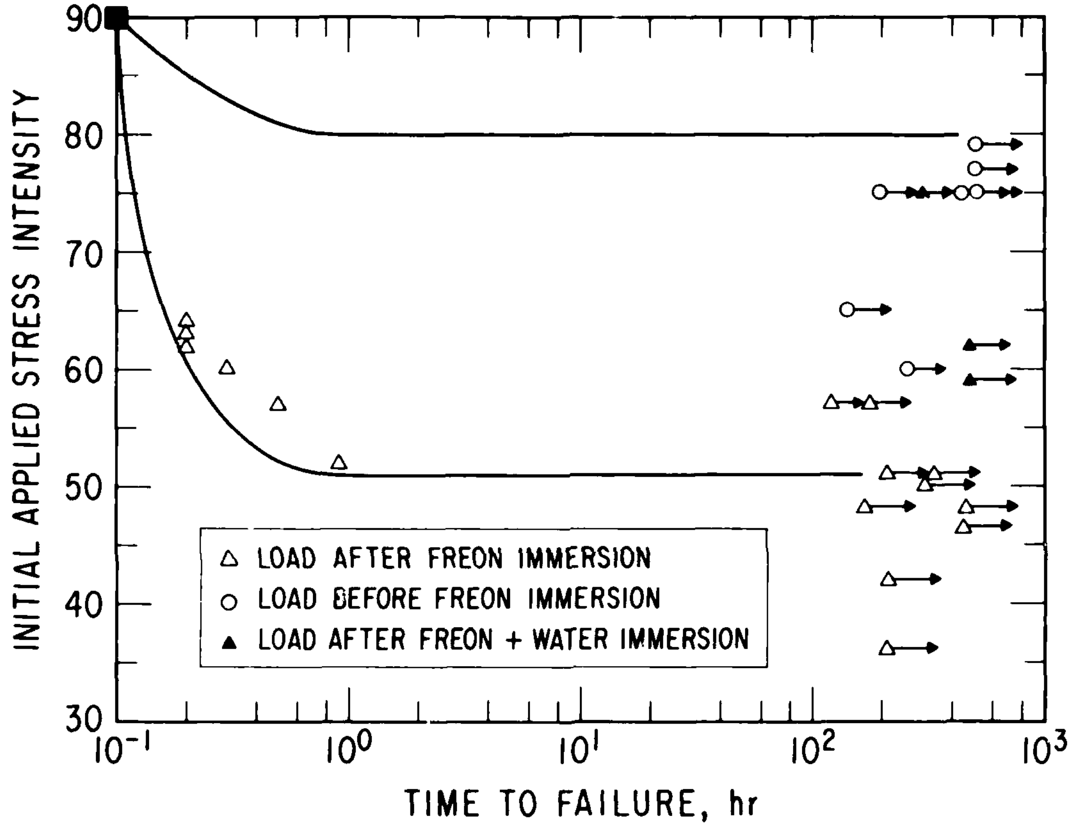

Figure 2. Ti-6Al-4V Exposed to Freon MF

Table 2. Freon MF and Freon MF + Cl_2 Mechanical Data

Specimen No.	Initial Crack Length in.	Initial Load lb	Initial K_c ksi$\sqrt{in.}$	Critical Crack Length in.	Critical Load lb	Critical K_c ksi$\sqrt{in.}$	Net Failure Stress ksi
1A	0.268	1200	36.0	-	-	-	-
1B	0.335	1580	62.0	0.44	1580	95.0	61
2A	0.267	1400	42.0	-	-	-	-
2B	0.335	1450	57.0	0.370	1900	86.0	65
3A	0.257	1600	46.5	-	-	-	-
3B	0.300	1740	60.0	0.380	1740	82.0	60
4	0.250	2000	57.0	0.40	2000	100.0	72
5	0.254	1800	52.0	0.39	1800	89.5	64
6	0.262	1800	54.0	0.40	1800	90.0	65
7A	0.264	1600	48.0	-	-	-	-
7B	0.325	1300	48.0	0.360	2525	111.0	85
8A	0.230	1400	37.0	-	-	-	-
8B	0.300	1400	48.0	-	-	-	-
8C	0.360	1380	60.0	-	-	-	-
8D	0.390	1600	80.0	-	-	-	-
9	0.320	1550	57.0	0.330	2000	76.0	64
10	0.300	1650	57.0	0.335	2080	83.0	67
11	-	-	-	0.270	2880	88.0	85
12	-	-	-	0.280	2870	92.0	86
13	-	-	-	0.250	3250	93.0	93
14	-	-	-	0.250	2800	79.0	80
15	-	-	-	0.270	2950	88.0	87
16	-	-	-	0.250	3050	86.0	87
17	0.235	2340	64.0	0.380	2150	101.0	75
18	0.250	2200	63.0	0.370	2070	94.0	71
19	0.250	2150	62.0	-	-	-	-
20A	0.280	1560	50.0	-	-	-	-

Table 2. Freon MF and Freon MF + Cl_2 Mechanical Data (Concluded)

Specimen No.	Initial Crack Length in.	Initial Load lb.	Initial K_c ksi$\sqrt{in.}$	Critical Crack Length in.	Critical Load lb	Critical K_c ksi$\sqrt{in.}$	Net Failure Stress ksi
20B	0.330	1720	65.0	-	-	-	-
21A	0.225	2000	51.0	-	-	-	-
21B	0.280	2320	75.0	-	-	-	-
22A	0.240	1880	51.0	-	-	-	-
22B	0.330	2200	83.0	-	-	-	-
23A	0.230	2000	51.0	-	-	-	-
23B	0.265	2330	70.0	-	-	-	-
23C	0.330	1710	65.0	-	-	-	-
24A	0.260	2000	60.0	-	-	-	-
24B	0.340	2050	78.0	-	-	-	-
25A	0.260	2160	65.0	-	-	-	-
25B	0.320	2120	79.0	-	-	-	-
26A	0.280	2320	73.0	-	-	-	-
26B	0.340	2120	85.0	-	-	-	-
27A	0.230	2750	73.0	-	-	-	-
27B	0.270	2400	73.0	-	-	-	-
28	0.220	2800	73.0	-	-	-	-
29	0.220	2640	69.0	-	-	-	-
30	0.240	2000	52.0	-	-	-	-
31A	0.210	2300	60.0	-	-	-	-
31B	0.352	1480	63.0	-	-	-	-
33A	0.190	2920	75.0	-	-	-	-
33B	0.437	1280	75.0	-	-	-	-
34A	0.200	2880	75.0	-	-	-	-
34B	0.389	1180	58.0	-	-	-	-
35	0.260	2700	77.0	-	-	-	-
36	0.240	2760	79.0	-	-	-	-

Table 3. Freon MF and Freon MF + Cl_2 Environmental Data

No.	Environment and Comments	Freon Chemistry (ppm)							
		Before				After			
		H_2O	Cl^-	Cl_2	Ti	H_2O	Cl^-	Cl_2	Ti
1A	Freon MF for 208 hr	8.2	0.05	0	0	-	-	-	-
1B	Freon MF + Cl_2 broke in 0.2 hr	21.6	-	92.3	0	-	-	-	-
2A	Freon MF for 209 hr	23.8	0.07	0	0.48	23.8	0.07	0	0
2B	Freon MF for 164 hr, broken in Instron in air	-	-	-	-	17.7	0.52	0	0
3A	Freon MF for 451 hr	18.9	0.07	0	0	15.9	0.07	0	0
3B	Freon MF broke in 0.3 hr	30.0	0.05	0	0	-	-	-	-
4	Freon MF broke in 0.5 hr	-	-	-	-	28.1	0.05	0	tr
5	Freon MF broke in 0.9 hr	-	-	-	-	14.6	0.05	0	0
6	Freon MF + Cl_2 broke in 0.7 hr	8.0	-	97.0	tr	10.8	-	99.0	tr
7A	Freon MF + Cl_2 for 237 hr	15.0	-	97.0	0	-	-	-	-
7B	Freon MF for 460 hr, broken in Instron in air	22.8	0.04	0	0	14.4	0.05	0	0.17
8A	Freon MF + Cl_2 for 235 hr	8.0	-	66.5	0	-	-	-	-
8B	Freon MF for 173 hr	34.0	<0.02	-	tr	36.6	0.13	0	tr
8C	Air for 3.8 hr, Freon MF + Cl_2 for 287 hr	-	-	99.1	-	55.3	3.9	0	0
8D	Air for 4 hr, Freon MF + Cl_2 broke in 65.7 hr	-	34	60.8	-	-	-	-	-
9	Freon MF + Cl_2 for 120 hr broken in Instron in air	-	-	99.1	-	14.7	7.9	2.5	0
10	Freon MF for 120 hr, broken in Instron in air	-	-	-	-	20.8	0.12	0	0
11	Broken in Instron in air	-	-	-	-	-	-	-	-
12	Broken in Instron in air	-	-	-	-	-	-	-	-
13	Broken in Instron in air	-	-	-	-	-	-	-	-
14	Broken in Instron in air	-	-	-	-	-	-	-	-
15	Broken in Instron in air	-	-	-	-	-	-	-	-

Table 3. Freon MF and Freon MF + Cl_2 Environmental Data (Continued)

No.	Environment and Comments	Freon Chemistry (ppm)							
		Before			After				
		H_2O	Cl^-	Cl_2	Ti	H_2O	Cl^-	Cl_2	Ti
16	Broken in Instron in air	-	-	-	-	-	-	-	-
17	Freon MF, crack growing rapidly at 0.1 hr Broken in Instron in air	6.1	-	-	-	29.4	3.0	0	tr
18	Freon MF, crack growing rapidly at 0.1 hr Broken in Instron in air	6.1	-	-	-	26.2	0.04	0	tr
19	Freon MF, crack growing rapidly at 0.1 hr	-	-	-	-	15.3	-	0	0
20A	Freon MF for 310 hr	18.2	-	-	-	44.1	0.06	0	tr
20B	Air for 4.1 hr, Freon MF + Cl_2 for 286 hr	-	34.0	60.8	-	26.0	6.6	0.6	tr
21A	Freon MF + Cl_2 for 211 hr	-	<0.5	25.0	0	21.3	6.4	1.4	tr
21B	Air for 1.5 hr, Freon MF + Cl_2 broke in 75hr	33.8	-	60.7	0	3.9	8.0	6.7	0
22A	Freon MF for 334 hr	16.9	<0.02	-	tr	63.1	1.84	0	0
22B	Air for 0.6 hr, Freon MF + Cl_2 broke in 0.2 hr	33.8	-	60.7	0	-	-	-	-
23A	Freon MF for 211 hr	16.9	<0.02	0	tr	22.4	0.05	0	0
23B	Air for 1.5 hr, Freon MF for 161 hr	103.0	<0.02	0	0	29.3	0.09	0	0
23C	Air for 4 hr, Freon MF + Cl_2 broke 25.4 hr	34.0	-	60.8	0	-	-	-	-
24A	Air for 4.4 hr, Freon MF for 264 hr	17.4	0.09	0	-	18.9	<0.02	0	0
24B	Air for 0.6 hr, Freon MF + Cl_2 broke in 3.3 hr	-	-	60.8	0		-	-	-
25A	Air 6.8 hr, Freon MF for 140 hr unload. Reload in 10 min for 149 hr	17.4	0.09	0	-	-	-	-	-

Table 3. Freon MF and Freon MF + Cl_2 Environmental Data (Concluded)

No.	Environment and Comments	Freon Chemistry (ppm)							
		Before			After				
		H_2O	Cl^-	Cl_2	Ti	H_2O	Cl^-	Cl_2	Ti
25B	Air for 0.5 hr, Freon MF + Cl_2 broke in 1.5 hr	-	-	60.8	0	-	-	-	-
26A	Air for 4.7 hr, Freon MF for 198 hr	17.4	0.09	0	-	-	-	-	-
26B	Air for 2.1 hr, Freon MF + Cl_2 broke in 46 hr	-	-	-	-	13.0	12.1	8.5	tr
27A	Air 4.1 hr, Freon MF for 330 hr	17.4	0.09	0	-	20.2	0.04	0	tr
27B	Freon MF broke in 0.2 hr	7.1	0.07	0	-	-	-	-	-
28	Air for 3 hr, Freon MF + Cl_2 broke 4 hr time 27.6 hr	21.5	-	67.0	0	-	-	-	-
29	Air for 2.9 hr, Freon MF + Cl_2 broke 12.1 hr	21.5	-	67.0	0	4.5	20.3	19.7	tr
30	Freon MF + Cl_2 for 1030 hr	21.5	-	67.0	0	-	-	-	-
31A	Air for 4 hr, Freon MF + Cl_2 for 980 hr	16.7	25.8	38.2	tr	-	-	-	-
31B	Freon MF water saturated for 471 hr	~90.0	-	-	-	-	-	-	-
33A	Air for 4 hr, Freon MF for 980 hr	26.3	0.02	0	0	0	-	-	-
34A	Air for 4 hr, Freon MF for 790 hr	-	-	-	-	-	-	-	-
34B	Freon MF + water for 260 hr	~90.0	-	-	-	-	-	-	-
35	Air for 4 hr, Freon MF for 790 hr	-	-	-	-	-	-	-	-
36	Air for 4 hr, Freon MF for 790 hr	-	-	-	-	-	-	-	-

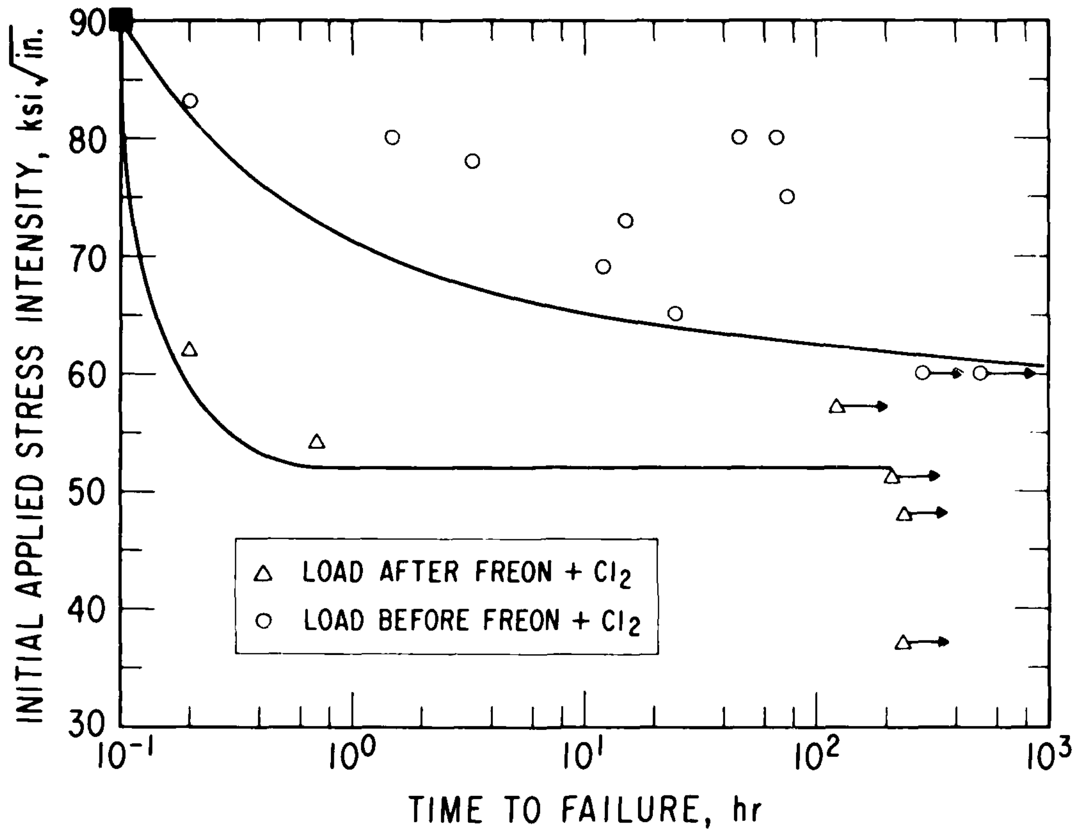

Figure 3. Ti-6Al-4V Exposed to Freon MF + Cl_2

A comparison of Figs. 2 and 3 shows that the behavior of specimens loaded in air for several hours prior to exposure to chlorinated Freon MF is distinctly different from the behavior of those exposed to commercial Freon MF. Failure times approaching 100 hr were observed for specimens exposed to chlorinated Freon MF. It is believed that K_{th} is unaffected by the loading sequence, although it would be difficult to prove because of the lengthy failure times involved.

The fracture surfaces indicate something of the nature of the Freon MF attack. As previously mentioned, fatigue precracks are introduced prior to loading the specimens; if the applied K_c is above the threshold value, the crack advances to the critical crack length, resulting in catastrophic fracture. Figure 4 shows that the crack advanced due to fatiguing in region A. The plane of the crack advance is at right angles to the length direction of the specimen. In region B, the crack advanced because of environmentally induced flaw growth. Again, the plane of crack advance is at right angles to the length direction of the specimen. The fracture surface is "brittle" in nature with many flat facets. In region C, the crack advanced rapidly (catastrophic failure) with the plane of the fracture at 45-deg angles to both the length and thickness (shear mode).

Figure 5 is an electron fractograph taken from the region of environmentally induced crack growth. The Freon MF attack results in a cleavage-dimple rupture fracture surface as was observed in other investigations of flaw growth in Ti-6Al-4V in nonaqueous environments.[15]

B. FREON TF AND FREON TF + Cl_2

Fatigue precracked, single-edge notched specimens were used for this phase of the study. These specimens were 0.090-in. thick by 0.50-in. wide and were loaded at a head displacement rate of 0.02 in./min in air. For this material thickness under these conditions, K_c was found to be 58 ksi-$\sqrt{\text{in.}}$ $\pm$ 10% (specimens 4 to 9). Load-versus-crack openings were determined to detect pop-ins. No pop-ins were noted.

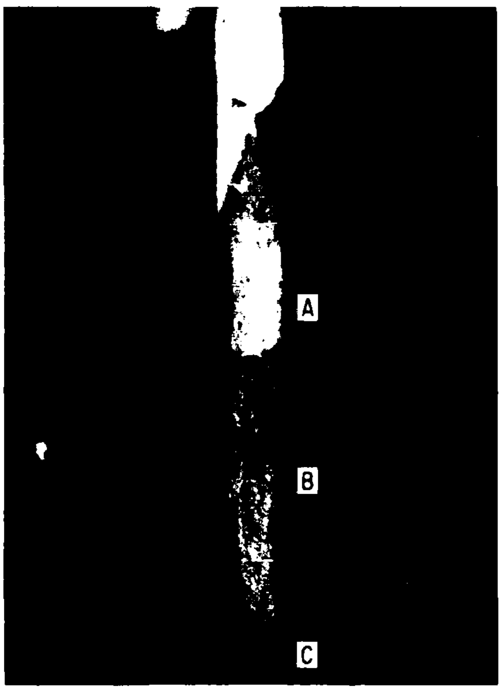

Figure 4. Fracture Surface of a Specimen Exposed to Freon MF 8X

Figure 5. Fractograph of Specimen Exposed to Freon MF 4000X

For specimens exposed to Freon TF, no delayed failures were observed. K_{th}/K_c is unity within the experimental error of ± 10%. The data are listed in Tables 4 and 5.

For specimens exposed to chlorinated Freon TF, time-to-failure versus initial applied K_c is plotted in Fig. 6; the data are listed in Table 3. Figure 6 shows that K_{th}/K_c is 0.85. Direct evidence of the attack is provided by Fig. 7. The environmentally induced crack growth region (B) is plainly visible ahead of the fatigue region (A). Region C fractured rapidly.

Table 4. Freon TF and Freon TF + Cl_2 Mechanical Data

Specimen No.	Initial Crack Length in.	Initial Load lb	Initial K_c ksi$\sqrt{in.}$	Critical Crack Length in.	Critical Load lb	Critical K_c ksi$\sqrt{in.}$	Net Failure Stress ksi
1	-	-	-	-	-	-	-
2	-	-	-	0.302	1410	93	77
3	-	-	-	0.060	5770	67	144
4	-	-	-	0.119	3170	63	90
5	0.110	2200	40	0.110	3550	64	99
6	0.150	2000	49	0.150	2600	64	82
7	-	-	-	0.140	2200	50	67
8	-	-	-	0.120	3000	59	87
9	-		-	0.070	4000	51	102
10	0.180	1700	53	0.235	1700	84	70
11	0.170	1800	52	0.215	1800	73	70
12	0.180	1600	50	0.180	2720	85	93
13	0.140	2160	50	0.200	2160	78	79
14	0.175	1740	52	0.175	3260	97	110
15	0.210	1260	46	0.210	2620	95	100
16	0.140	1720	40	0.140	3200	73	70

Table 5. Freon TF and Freon TF + Cl_2 Environmental Data

No.	Environment and Comments	Freon Chemistry (ppm)							
		Before				After			
		H_2O	Cl^-	Cl_2	Ti	H_2O	Cl^-	Cl_2	Ti
1	Broken while precracking	-	-	-		-	-	-	-
2	Not meaningful because crack too deep	-	-	-	-	-	-	-	-
3	Not meaningful because net stress too high	-	-	-	-	-	-	-	-
4	Broken in air	-	-	-	-	-	-	-	-
5	Freon TF for 120 hr then broken in Instron in air	64	0	0	0	40.0	0	0	0
6	Freon TF for 772 hr then loaded to failure in Freon TF	26	0	0	0	28.5	0.07	0	0.1
7	Broken in Instron in air	-	-	-	-	-	-	-	-
8	Broke in sec in Freon TF	-	-	-	-	-	-	-	-
9	Broke in sec in Freon TF	-	-	-	-	-	-	-	-
10	Freon TF + Cl_2. Broke in 18 hr	18	-	62.0	-	-	-	-	-
11	Freon TF + Cl_2. Broke in 18 hr	18	-	62.0	-	-	-	-	-
12	Freon TF + Cl_2 for 1845 hr	18	-	62.0	-	36.0	-	-	3.1
13	Freon TF + Cl_2. Broke in 41 hr	21	-	15.1	-	39.0	-	7.5	-
14	Freon TF for 1750 hr then broken in Instron	-	-	-	-	-	-	-	-
15	Freon TF + Cl_2 1585 hr then broken in Instron	22	-	56.0	-	36.0	-	0.51	
16	Step Loaded in air	-	-	-	-	-	-	-	-

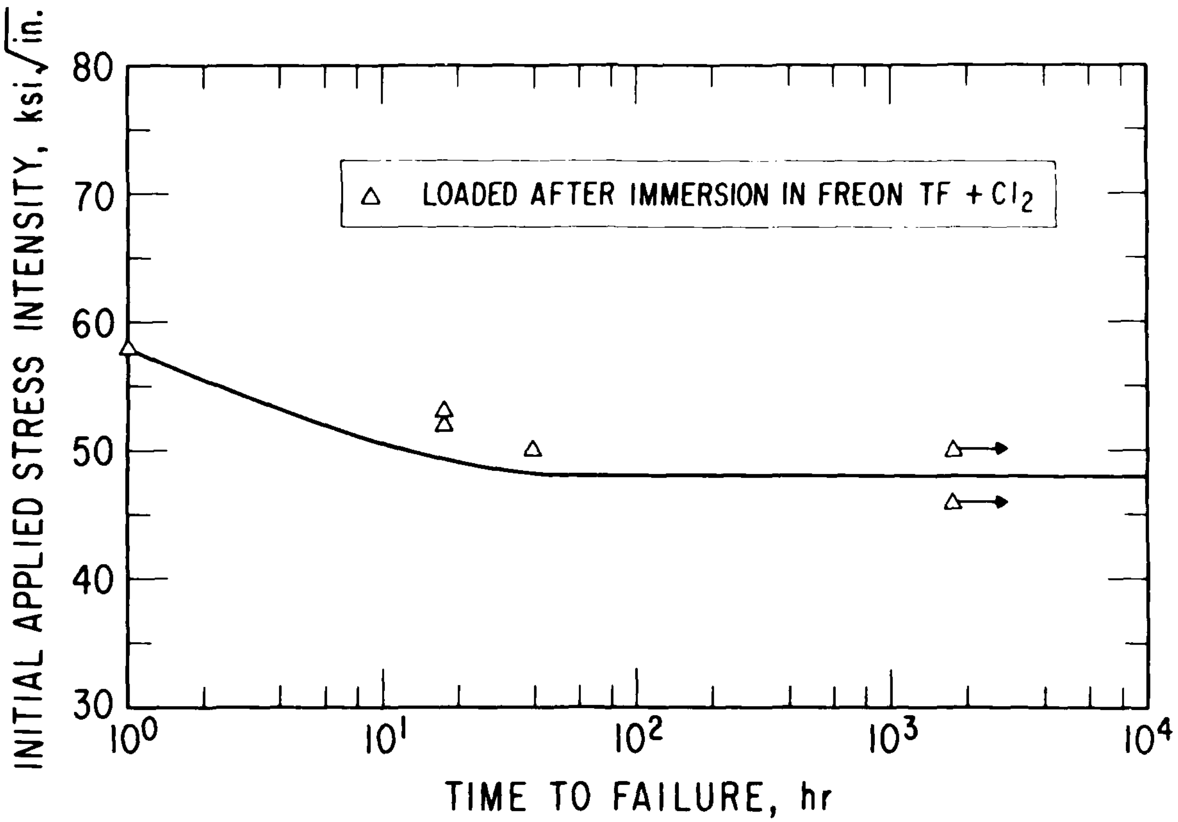

Figure 6. Ti-6Al-4V Exposed to Freon TF + Cl_2

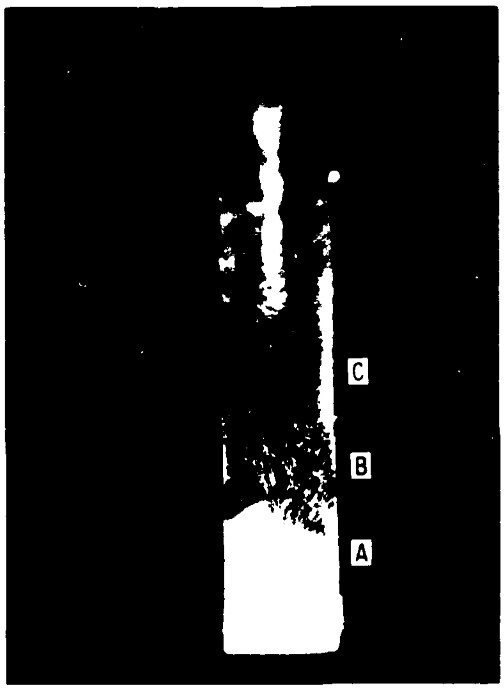

Figure 7. Fracture Surface of
Specimen Exposed to
Freon TF 4X

VI. DISCUSSION OF RESULTS

The data shown in Fig. 2 indicate that the primary function of the stress intensity at the crack tip is to expose fresh titanium metal to the Freon MF environment and to keep the crack moving sufficiently fast that repassivation does not occur. The specimens loaded in air for several hours prior to exposure to Freon MF were unaffected for applied stress intensity values approaching K_c. Presumably, an oxide coating protected the crack tip. For specimens loaded in the Freon MF environment, applied stress intensity values greater than 0.57 K_c were sufficiently high to initiate and sustain the Freon MF attack. The higher oxidation power of the water-saturated Freon MF environment protected the crack tip from attack.

The effect of chorine additions on the titanium-Freon MF interaction may be seen by comparing Figs. 2 and 3. The oxide film that formed during preload in air and protected the crack tip from Freon MF did not protect the crack tip from chlorinated Freon MF. The applied stress intensity versus time-to-failure behavior for the specimen preloaded in air and exposed to chlorinated Freon MF is distinctly different from the other data. The remaining three curves of Figs. 2 and 3 contain no failure times in excess of 1 hr; however, failure times approaching 100 hr were recorded for the specimens preloaded in air and exposed to chlorinated Freon MF. Very little of this long failure time could be attributed to crack propagation; most of the time was consumed in attack of the oxide coating. Presumably, the principal damaging function of the chlorine is to aid the degradation of the oxide coating since the threshold stress intensity value is essentially the same for both Freon MF environments.

The preceding observations are consistent with recent observations of stress-corrosion of titanium alloys in nonaqueous environments; however, the precise atomic mechanisms operative are yet to be clearly determined.[16-18]

Powell and Scully[16] studied the interaction of a titanium alloy with methanol/HCl mixtures and concluded that the attack was a form of hydrogen embrittlement producing cleavage. The critical step is the exposure of bare metal to the environment. The reaction (unspecified) discharges hydrogen into the metal. The reformation of the passive film is an important parameter because the film is nearly impervious to hydrogen. Powell and Scully show that repassivation depends on the ratio of passivating (H_2O) to active species at the crack tip.

Haney, et al.[17] investigated the stress corrosion of titanium alloys in halogenated methanol-water solutions and suggest an electrochemical mechanism of dissolution along an active path. Anodic polarization of specimens decreased the time-to-failure, while small cathodic current densities significantly increased the time-to-failure. This behavior is definitely not consistent with a mechanism of hydrogen embrittlement. In this investigation, the importance of water as a passivating agent was demonstrated. It was found that halogen ions (Cl^-, Br^-, I^-) were necessary to the attack, but the exact nature of their contribution is uncertain. It is possible that local hydrolysis of the halogen produces acid conditions and that the acid dissolves the passive film.[18]

Discussion of the precise atomic mechanisms involved in the Freon MF attack of Ti-5Al-4V may be considered moot for this investigation since none of the data allows one to differentiate between hydrogen embrittlement and anodic dissolution. The effects of water content and chlorine concentration suggest that control of this ratio of water/chlorine may be an effective way to prevent Freon MF degradation of the flaw-bearing properties of Ti-6Al-4V.

VII. CONCLUSIONS

This study indicates that the primary function of stress-intensity in the Ti-6Al-4V/Freon MF interaction is the exposure of fresh titanium surfaces to the environment through plastic deformation at the crack tip.

The chief damaging role of chlorine additions to the Freon environment is to aid degradation of the passive coating at the crack tip. The beneficial effect of high water contents (90 ppm) in the Freon environment is to increase the repassivation reaction.

The exact atomic mechanism of the Ti-6Al-4V/Freon interaction is uncertain, but maintaining a high water/chlorine content ratio is expected to obviate burst failures.

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13 ABSTRACT

The general and stress corrosion behavior of Ti-6Al-4V alloy in Freon environments were investigated. Intentionally flawed specimens were examined to determine the ability of the metal to sustain defects on exposure to stress and environment. Freon TF and Freon MF were used as base environments for the study. In addition to testing with commercially pure Freons, chlorine-doped Freons were used. Two thicknesses of solution-treated and aged Ti-6Al-4V alloy were used. The crack-bearing properties of a metal in the presence of an environment is based on the framework of fracture mechanics.

It is indicated that the primary function of stress-intensity in the Ti-6Al-4V/Freon MF interaction is the exposure of fresh titanium surfaces to the environment through plastic deformation at the crack tip.

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