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⑥ THE STRESS-CORROSION AND ACCELERATED CRACK-PROPAGATION BEHAVIOR OF TITANIUM AND TITANIUM ALLOYS .

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⑩ J. D. Jackson W. K. Boyd

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Roger J. Runck
Director

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TABLE OF CONTENTS

Page

THE STRESS-CORROSION AND ACCELERATED CRACK-PROPAGATION BEHAVIOR OF TITANIUM AND TITANIUM ALLOYS

J. D. Jackson and W. K. Boyd

SUMMARY

This technical note summarizes information which has become available to DMIC on the stress-corrosion cracking and crack propagation behavior of titanium alloys in a variety of environments. Much of this information, particularly that regarding accelerated crack propagation in aqueous and liquid solutions, is preliminary and the conclusions offered herein should be viewed as tentative and subject to change as additional information becomes available.

Almost all titanium alloys are susceptible to stress-corrosion cracking at elevated temperatures in chloride salts. This reaction shows a time-temperature-stress dependency in which the critical values of these three parameters vary significantly among the different titanium alloys. In general, most alloys show their greatest susceptibility at temperatures from 550 F through 800 F although at least one susceptible alloy has shown some degradation of properties after an exposure of 6400 hours at temperatures slightly above 400 F and a stress of about 61 ksi. For an exposure period of 100 hours, the threshold stress necessary to initiate salt-corrosion cracking varies from 20 to 100 ksi at 550 F to values from less than 5 to 50 ksi at 800 F, depending on alloy composition and heat treatment.

The mechanism of hot-salt stress-corrosion cracking apparently involves sodium chloride, oxygen, water, and reaction products of titanium dichloride, sodium hydroxide and titanium dioxide. Cyclic exposure from room temperature to test temperature greatly reduces the susceptibility to hot-salt stress-corrosion cracking. Silver and silver compounds may cause stress-corrosion cracking of titanium alloys at 700 F and above. A type of stress-corrosion cracking has also been observed in liquid nitrogen tetroxide at 105 F. Solutions of methyl alcohol containing hydrochloric or sulfuric acids also crack titanium as does contact with liquid mercury and molten cadmium. Titanium and its alloys also suffer severe stress-corrosion cracking and/or pyrophoric reaction in dry, red fuming nitric acid.

Through the use of new experimental techniques, accelerated crack propagation of precracked titanium specimens has been observed in certain environments in which titanium had previously shown little or no corrosion. This technique in essence eliminates the initiation step and provides a more rapid means of evaluating susceptibility to stress-corrosion cracking under simulated service conditions.

INTRODUCTION

While the susceptibility of titanium alloys to stress corrosion by hot salt has been known since 1957,(1) renewed attention was focused on this problem when titanium alloys were first considered as candidate materials in supersonic transport (SST) aircraft. A critical review of the data available on this subject through the period of July, 1964, was given by Boyd and Fink in a NASA publication.(2) In 1965, considerable interest was aroused from the finding(3) that several precracked titanium alloys were subject to accelerated failure when stressed in some environments. This has since become a matter of concern to both the deep-diving submersible vehicle program (DDS) of the Navy as well as to the SST program.

It should be emphasized that neither of these phenomena are unique to titanium and its alloys. Nonetheless, it does appear that, under certain conditions, most titanium alloys are susceptible to failure in either or both of these environments. It is also quite clear that the problems imposed by stress-corrosion cracking and crack propagation in titanium alloys are not insurmountable. Finally, it should be recognized that much work is still in progress to completely define the critical parameters in the hot-salt stress-corrosion cracking and crack propagation of titanium alloys. These include programs with the full or partial support of the Air Force, Federal Aviation Agency, National Aeronautics Space Administration, and Navy. Emphasis in the current work is being devoted to determining which alloys and/or specific forms and conditions of heat treatment provide the least degree of susceptibility or highest degree of immunity to these forms of failure as well as to what mechanisms are involved. Until these programs are complete, a full and fair assessment of the hot-salt stress-corrosion cracking and crack-propagation susceptibility of titanium alloys in liquids will not be possible.

Despite this qualification, interest in these problem areas is widespread, and DMIC continues to receive numerous requests for information on the subject of the stress-corrosion cracking behavior of titanium. Consequently, this note was prepared to provide a brief summary of the reports and papers which have recently become available on this subject. In addition to information on stress-corrosion cracking by hot salt, this note also summarizes the available data on the stress-corrosion cracking behavior of titanium and its alloys in other media such as methyl alcohols, red fuming nitric acid, silver, cadmium, and mercury.

In compiling this information, DMIC gratefully acknowledges the permission of the American Society for Testing Materials to use selected data from a collection of 14 papers which were presented at the ASTM Pacific Area National Meeting in Seattle, Washington, on November 1-2, 1965. The complete collection of these papers is scheduled for publication by the ASTM as Special Technical Publication No. 397 on or about May 15, 1966.

HOT-SALT STRESS-CORROSION CRACKING

As noted previously, a review of the available data and proposed mechanisms of hot-salt stress-corrosion cracking were presented by Boyd and Fink(2) in 1964. The information reviewed here is intended to supplement that report. However, two related preliminary statements based on that report merit repeating here. The first is that the susceptibility of titanium alloys to stress-corrosion cracking by hot salt has largely been demonstrated through the use of a variety of laboratory tests. The second is that, to date, no aircraft service failures from hot-salt stress-corrosion cracking of titanium alloys have been reported even though these have been used extensively in air frames and jet engines at operating temperatures as high as 900 F.

Susceptible Alloys

It appears that most titanium alloys are susceptible to some degree to hot-salt stress-corrosion cracking. The alpha-phase alloys, such as Ti-5Al-2.5Sn, Ti-7Al-12Zr, and Ti-5Al-5Sn-5Zr, are apparently most susceptible to attack.(4) The alpha-beta alloys are less susceptible, and the degree of susceptibility may increase with increases in aluminum content.(4) For example, the Ti-8Al-1Mo-1V alloy (both as mill annealed and duplex annealed) is very susceptible. However, the Ti-8Mn alloy, which contains no aluminum, is also susceptible.

Alloys with intermediate resistance are Ti-5Al-5Sn-5Zr-1Mo-1V, Ti-6Al-4V, Ti-6Al-6V-2Sn, Ti-5Al-2.75Cr-1.25Fe, and Ti-3Al-11Cr-13V. Among the most resistant alloys are Ti-4Al-3Mo-1V, Ti-2.5Al-1Mo-10Sn-5Zr, (IMI 679)(4) and an experimental Ti-2Al-4Mo-4Zr alloy.(5)

Effect of Temperature, Stress, and Time

Hot-salt stress-corrosion cracking of titanium alloys is a function of temperature, stress, and time of exposure. In very general terms, hot-salt stress-corrosion cracking has not been observed below about 500 F. The temperature range of greatest susceptibility is 550 F to 800 F, and within this range, time to failure is decreased as either the temperature or stress level is increased. There also appears to be an upper temperature limit at which general corrosion is so rapid as to mask any stress corrosion cracking. These limits are about 800 F, 900 F, and 1000 F for the Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-7Al-12Zr alloys, respectively.(6)

These general effects of temperature, stress, and time are illustrated for the Ti-8Al-1Mo-1V alloy in Figure 1 which summarizes data reported prior to April, 1965.(7) Some inconsistencies are apparent in this figure and probably arise from differences in heat treatment and/or the test conditions that were used by the various sources. More recent information indicates, for example, that stress-corrosion cracking, per se, of titanium alloys "does not occur at 500 F, at least within 8000 hours", although it does occur at 525 F "under high stresses and long times".(5) Figure 2 shows some 1000 hour exposure data for several alloys which agree with this premise. On the other hand, other investigators have shown that some of the more susceptible alloys display susceptibility at temperatures below 500 F and times of less than 8000 hours. Specifically, Figure 3 from a NASA study(9) shows the changes in room-temperature ductility that were observed on residual stress specimens of duplex annealed Ti-8Al-1Mo-1V after

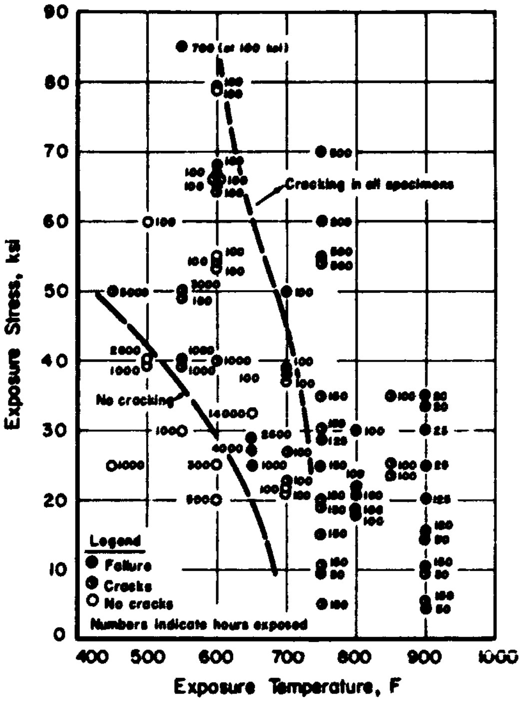


FIGURE 1. EFFECT OF EXPOSURE VARIABLES ON THE OCCURRENCE OF VISIBLE SALE STRESS-CORROSION IN Ti-8Al-1Mo-1V(7)

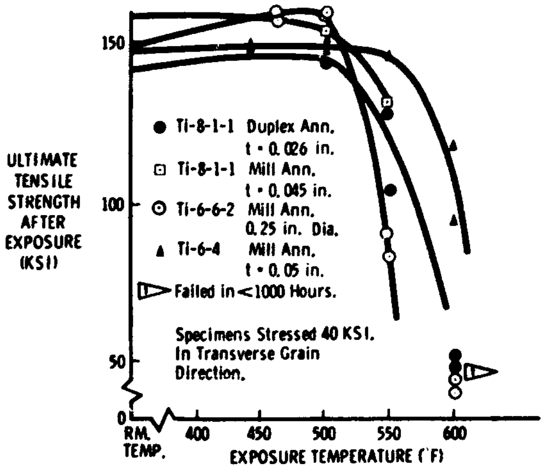


FIGURE 2. RESIDUAL STRENGTH OF TITANIUM ALLOYS AFTER EXPOSURE TO SODIUM CHLORIDE FOR 1000 HOURS(8)

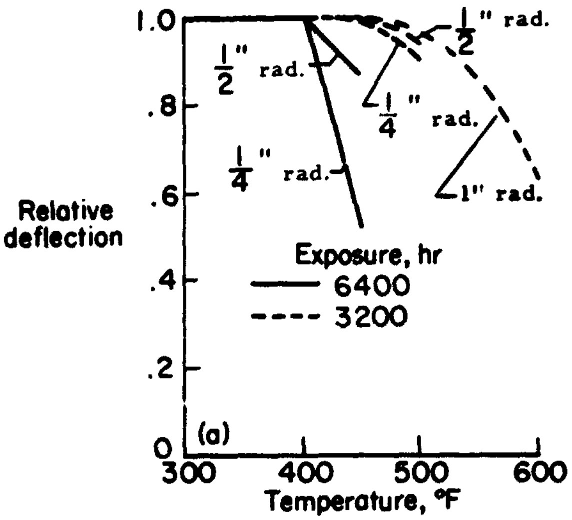


FIGURE 3. STRESS-TEMPERATURE THRESHOLDS FOR DUPLEX ANNEALED Ti-8Al-1Mo-1V RESIDUAL STRESS SPECIMENS(9)

Samples previously bent through radii shown, then salt coated and exposed at temperatures from 400 F to 600 F for times indicated, and bent to failure at room temperature.

exposures of 3200 and 6400 hours at temperatures down through 400 F. These results indicate that, for exposures of 6400 hours, some damage has occurred on the material exposed at temperatures slightly above 400 F.

The threshold stress, or stress above which hot-salt stress-corrosion cracking can occur, has been reported for several alloys using various time periods. For example, the approximate, short-time (100 hours) threshold values are shown in Table 1. Some discrepancies can be noted in the table. These may occur because of variations in experimental techniques, metallurgy, or heat treatments. These data are presented for information only, and are not necessarily indicative of service results.

Obviously, longer times at temperature will tend to reduce the threshold stress values. For example, the threshold stress of Ti-8Al-1Mo-1V is decreased by 50 percent at 850 F when the time increases from 100 to 1000 hours.(4) Experiments are presently being run for times of up to 30,000 hours, to duplicate anticipated SST service life.(11) Results after times to 20,000 hours are summarized in Table 2. Note that failures have also occurred with specimens which were silver brazed but not salt coated. This stress-corrosion cracking is caused by silver and silver salts, as discussed in another section. As indicated in Table 2, no hot-salt failures have been observed for Ti-6Al-4V after 20,000 hours at 550 F and up to 58 ksi stress.

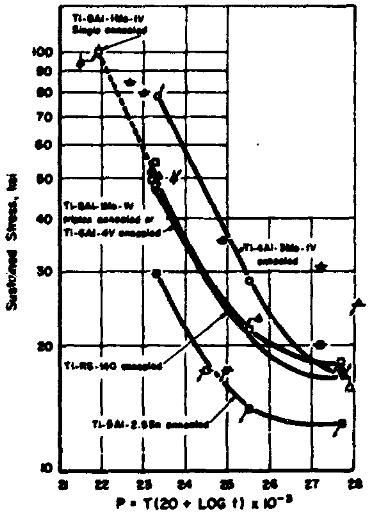


FIGURE 4. APPLICATION OF LARSEN-MILLER PARAMETER FOR PREDICTING STRESS-CORROSION CRACKING BY HOT SALT OF ANNEALED TITANIUM ALLOYS(10,12)

The combined effects of time, temperature, and stress for several titanium alloys are shown in Figure 4,(10,12) which represents data from many sources. These data suggest the stress-corrosion cracking thresholds for the various alloys. This plot employs the empirical Larsen-Miller parameter, originally used for generalizing creep data in steel.(13) Excellent agreement is indicated for the data. From this plot, the estimated threshold stress for hot-salt cracking at 550 F and 30,000 hours is 45,000 psi for Ti-4Al-3Mo-1V (annealed), 30,000 psi for Ti-8Al-1Mo-1V (triplex annealed) and Ti-6Al-4V (annealed), 28,000 psi for Ti-5Al-2.75Cr-1.25Fe (annealed) and 18,000 psi for Ti-5Al-2.5Sn (annealed).

The ductility of titanium alloys is also reduced after long-time exposure to hot salt. This has been shown, for example, in a NASA study(14) where mill-annealed Ti-8Al-1Mo-1V sheet and various other titanium alloy sheets were exposed at 550 F for times up to 7000 hr at 50 and 100-ksi stress levels. These were salt coated, restrained bend specimens which after exposure were bent to smaller radii until failure occurred (see reference for test details). For convenience of measurement, chord length was measured at the point of specimen failure which was then compared with chord length (i.e., as a measure of deformation) of salt-free exposed samples. A summary of the results obtained in this study is given in Figure 5. The experiments indicate the relatively high susceptibility of mill-annealed Ti-8Al-1Mo-1V alloy under these conditions.

TABLE 1. APPROXIMATE THRESHOLDS FOR STRESS-CORROSION CRACKING OF TITANIUM ALLOYS IN HOT SALT

		100 Hr Threshold Stress, ksi									
	Condition	550	600	650	700	750	800	850	900	950	Reference
Ti-4Al-3Mo-1V	Aged	-	95	-	25	-	25	-	-	-	10
	Annealed	84	78	-	28	-	15-49	-	-	-	10, 5
Ti-2.5Al-1Mo-10Sn-5Zr	Aged	-	-	-	70	-	40	-	35	-	4
Ti-5Al-5Sn-5Zr-1Mo-1V		69	-	-	-	-	35	-	-	-	5
Ti-6Al-4V	Aged	-	95	65	25	30	12	15	-	-	10, 4
	Annealed	50	50	-	22	-	18-24	-	-	-	10, 5
Ti-5Al-2.75Cr-1.25Fe	Aged	-	80	-	25	-	18	-	-	-	10
	Annealed	-	45	-	-	-	15	-	-	-	10
Ti-8Al-1Mo-1V	Aged	-	-	-	-	25	-	20	-	15	4
	Annealed	25	55	-	23	-	18	-	-	-	10, 5
Ti-5Al-2.5Sn	Annealed	28	30	-	15	-	10-20	-	-	-	10, 5
Ti-7Al-12Zr		-	-	-	-	-	<5	-	-	-	4
Ti-5Al-5Sn-5Zr		-	-	-	-	-	<5	-	<5	-	4

TABLE 2. ROOM-TEMPERATURE TENSILE PROPERTIES OF TITANIUM ALLOYS AFTER 650 F EXPOSURE(11)

Environment	Exposure Time, Hrs	Number of Tests	Number of Failures	Yield Strength, ksi	Elongation, percent
		Ti-8Al-1Mo-1V Mill Annealed(1)			
Air	20,000	3	None	126-136	17-20
Snythetic Sea Salt(2)	2,600-10,000	3	3	129-140	15
Silver Braze(3)	9,000-18,500	5	5	107-133	1-14
Braze and Salt	9,600-18,500	3	3	55-123	0-9
Syntnetic Sea Salt(4)	20,000	3	None	131-137	18-20
None	-	2	-	133	13.6
		Ti-6Al-4V, Solution-Treated and Aged(1)			
Air	20,000	3	None	132-160	14-15
Synthetic Sea Salt	20,000	3	None	146-158	14-18
Silver Braze	5,500-10,000	4	4	118-131	8
Braze and Salt	7,000-15,000	3	3	116-138	9-11
Synthetic Sea Salt(4)	20,000	3	None	132-153	14-15
None	-	1	-	125	15

(1) Specimens are cantilever type: stress varies from 23-37 ksi for Ti-6Al-4V and 23-31 ksi for Ti-8Al-1Mo-1V when unnotched or 45-58 ksi for Ti-6Al-4V and 56-67 ksi for Ti-8Al-1Mo-1V when notched.

(2) Six parts NaCl - 1 part $MgCl_2$.

(3) Dynabraze B - 94.8Ag-5Al-0.2Mn.

(4) Alternate exposure: 2 weeks 650 F air - 2 weeks water saturated air at 100 F.

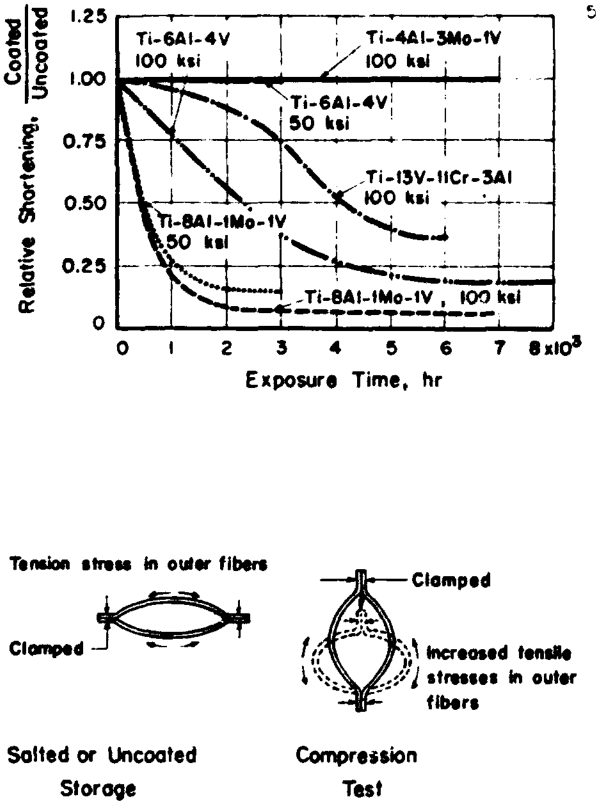


FIGURE 5. EFFECT OF TIME AND STRESS ON THE 550 F SALT-STRESS-CORROSION DEGRADATION OF PROPERTIES OF SELECTED TITANIUM ALLOYS(14)

Effect of Type of Salt

In preliminary work on the hot-salt problem, it was reported that the ASTM synthetic sea salt consisting of 7 parts NaCl and 1 part of $MgCl_2$ appeared to be more agressive than sodium chloride in causing hot-salt problems.(2,15) This was believed true because of the higher ionic conductivity and lower melting point of the synthetic salt. Recent studies have shown, however, that NaCl may actually be slightly more severe and that $MgCl_2$ content may not be a critical factor.(5,16) The indication that salts containing $MgCl_2 \cdot 6H_2O$ were more severe could have been caused by the water of hydration, since water is apparently necessary for hot-salt cracking as discussed later. In addition, thin salt coatings are more damaging, because the oxygen necessary for the attack can penetrate thin coatings easier. To date, the salt coating thicknesses have not been standardized among investigators.

The relative cracking effect of several salts on the Ti-8Al-1Mo-1V is shown in Figure 6.(9) This shows the loss of ductility after exposure at 600 F of samples that were residually stressed (by bending over a 1/4-inch radius) to 66 ksi, then bent to failure after exposure. Sodium chloride had the most severe effect followed by $7NaCl-1MgCl_2$ and sea salt, in that order. $MgCl_2$, by itself, caused only a slight loss of ductility. These results have been confirmed by others.(8,17)

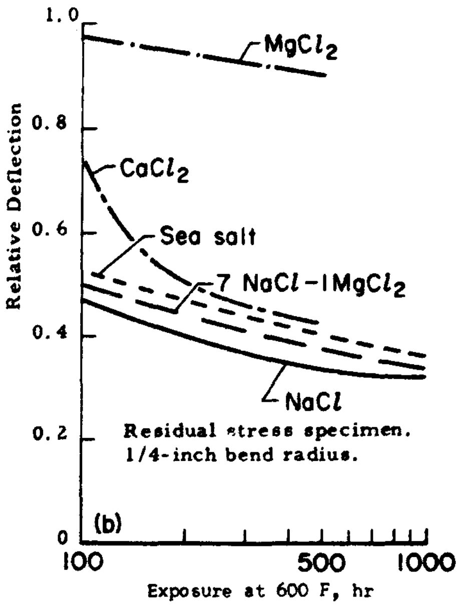


FIGURE 6. EFFECT OF TYPE OF SALT ON STRESS CORROSION OF DUPLEX ANNEALED Ti-8Al-1Mo-1V ALLOY SHEET AT 600 F(9)

A number of titanium alloys were examined for susceptibility to salt stress-corrosion cracking in a fairly comprehensive study(10) directed jointly by ASD, FAA, and NASA and conducted at Douglas Aircraft Company, McDonnell Aircraft Corporation and with support work elsewhere. Included in this work was an evaluation of various alloys to stress-corrosion attack by synthetic sea salt in which the variables studied covered alloy heat treatment, grain direction, sheet thickness, anodizing, and welding. Figure 7 is a summary of the findings after creep-tension exposures. Based on the maximum stress at which no stress-corrosion cracking was apparent in 100 hr, the alloys were rated in order of decreasing resistance to stress corrosion as follows:

At 600 F

(1) Ti-6Al-4V aged
Ti-4Al-3Mo-1V aged
Ti-4Al-3Mo-1V annealed
(2) Ti-5Al-4FeCr aged
(3) Ti-8Al-1Mo-1V triplex annealed
Ti-6Al-4V annealed
Ti-5Al-4FeCr annealed
(4) Ti-5Al-2.5Sn annealed

At 700 F

(1) Ti-4Al-3Mo-1V annealed
Ti-4Al-3Mo-1V aged
(2) Ti-6Al-4V aged
Ti-5Al-4FeCr aged
(3) Ti-8Al-1Mo-1V triplex annealed
Ti-6Al-4V annealed
(4) Ti-5Al-2.5Sn annealed

Alloy	Condition	600 F					700 F						800 F					
		Less than 50%	50%	65%	80%	Over 80%	Less than 50%		50%	65%	80%	Over 80%	Less than 50%		50%	65%	80%	Over 80%
6Al-4V	Annealed, .025 (actual stress, ksi)	27.0	38.5	50.1	61.6			21.7	31.0	40.3	49.6				17.7	22.9	28.2	
	Annealed, .025, longitudinal			N	0			N	0	0	X				N	X	X	
	Annealed, .025, transverse			N	0			N	0	0	X				N	X	X	
	Annealed, anodized, .025, transverse		0	0					X						X			
	Annealed, welded, .025, transverse	N	0	0				0	0						X			
	Annealed, .050 (actual stress, ksi)		42.9	56.7	68.6	85.4		24.1	34.5	44.9	55.2				19.7	25.5	31.4	
	Annealed, .050, transverse				N	0		0	X	0				N	X		X	
	Annealed, anodized, .050, transverse			N	0				0	0					N	X		
	Annealed, welded, .050, transverse				N				0	0					0		X	
	Aged, .025 (actual stress, ksi)		50.1	65.1	80.1	95.0		25.5	36.5	47.5	58.4			12.5	17.8	23.1	28.5	
	Aged, .025, longitudinal				N			N	X	X	X			N	X	X	X	
	Aged, .025, transverse				N	N		N	X	0				N	N	X	X	
5Al-2.5Sn	Annealed, .025 (actual stress, ksi)		29.8	38.7	47.6			14.2	28.3	36.7	45.2			10.3	20.6	26.8	33.0	
	Annealed, .025, longitudinal		N	0				0	X	X				N	X			
	Annealed, .025, transverse		N	X				0	X	X				X	X			
	Annealed, anodized, .025, transverse		N	0					X	X					X			
8Al-1Mo-1V	Annealed, .025 (actual stress, ksi)		41.8	54.3	66.8	79.3	21.7	27.0	38.5	50.1	61.6		18.3	21.0	30.0	39.0	48.0	
	Annealed, .025, longitudinal			0	0				N	X			X	0	X			
	Annealed, .025, transverse				0	N	N	0	0	X			X	X	X			
	Annealed, anodized, .025, transverse			N	0				0	X					X			
	Annealed, welded, .025, transverse			N	0		0		X	X					X			
	Annealed, .050 (actual stress, ksi)		41.8	54.3	66.8	79.3	21.7		38.5	50.1	61.6			21.0	30.0	39.0	48.0	
	Annealed, .050, transverse				N	0	N		X					X	X			
	Annealed, anodized, .050, transverse			N	0				X						X			
	Annealed, welded, .050, transverse		0	0	0				0						X			
4Al-3Mo-1V	Annealed, .025 (actual stress, ksi)		41.0	53.2	65.6	78.5			28.5	37.1	45.6	54.2			8.8	11.4	14.1	16.7
	Annealed, .025, longitudinal				N	N					N	X			N	N	N	N
	Annealed, .025, transverse				N	N			N	0	0				N	N	N	N
	Annealed, anodized, .025, transverse				N						N				N	N	N	
	Aged, .025 (actual stress, ksi)		48.5	63.1	77.6	92.3		26.4	36.3	47.1	58.0				16.0	20.8	25.6	30.4
	Aged, .025, longitudinal				N	N		N	0	X	X				N		N	X
	Aged, .025, transverse				N	N			0	X	X				N		N	N
RS-140	Annealed, .025 (actual stress, ksi)		36.0	46.8	57.6	68.4			16.5	21.5	26.4				10.5	13.7	16.8	
	Annealed, .025, longitudinal			N	0										N	N	N	
	Annealed, .025, transverse				N	X									N	N	N	
	Annealed, anodized, .025, transverse				N										N	N	N	
	Annealed, .050 (actual stress, ksi)		43.5	56.6	69.6	77.8			20.0	26.0	30.9				12.8	16.6	20.4	
	Annealed, .050, transverse				N	N										N	N	
	Annealed, anodized, .050, transverse			N	0											N	N	
	Aged, .025 (actual stress, ksi)		50.0	65.0	80.0	95.0		24.8	35.5	46.2	56.8			12.5	18.0	23.4	28.8	
	Aged, .025, longitudinal				N	0		N	X	X				N	N			
	Aged, .025, transverse				N	0		N	0	X				N	N			

X	One or more specimens failed during exposure.
0	No specimens failed but one or more had visible evidence of stress-corrosion cracking after exposure.
N	No specimens failed or had evidence of stress-corrosion cracking.

FIGURE 7. SUMMARY OF STRESS-CORROSION TEST RESULTS; SYNTHETIC SEA-SALT-COATED TITANIUM ALLOYS AT ELEVATED TEMPERATURE, 100 HR - SMOOTH SPECIMENS(10)

At 800 F

(1) Ti-4Al-3Mo-1V aged
(2) Ti-5Al-4FeCr aged
Ti-8Al-1Mo-1V triplex annealed
Ti-6Al-4V annealed
Ti-5Al-4FeCr annealed
Ti-4Al-3Mo-1V annealed
(3) Ti-6Al-4V aged
Ti-5Al-2.5Sn annealed.

Other salts which have been shown to cause damage to titanium alloys at elevated temperatures (100 hours at 750 F) are shown in Table 3.(6) NaI and NaBr are less harmful than NaCl, as are $CaCl_2$ and $MgCl_2$. The sulfides are less harmful than the chlorides. Na_2CO_3 and Na_2SO_4 appeared to have no effect.

TABLE 3. CHEMICALS CAUSING CRACKING OF TITANIUM ALLOYS, 100 HOURS 750 F.(6)

AgCl	$MgCl_2$	NaBr	H_2S
$BaCl_2$	NaCl	NaI	MoS
$CaCl_2$	$NiCl_3$		Na_2S
CCl_4	$SnCl_2$		
$FeCl_3$	$ZnCl_2$		
HCl	Chlorinated hydrocarbons		
KCl			
LiCl			

There is some evidence that sealing compounds used in aircraft construction may also cause stress-corrosion cracking at temperatures of the order of 500 F.(17) Many of these compounds contain chlorides, and some decomposition might be expected to cause stress-corrosion cracking.

Effect of Oxygen, Air Pressure, and Velocity

The necessity for oxygen in the hot-salt stress-corrosion cracking of titanium alloys has been reported by several investigators. For example, hot-salt stress-corrosion cracking of Ti-5Al-2.5Sn was readily observed at 800 and 900 F at an air pressure as low as 10 microns Hg. However, when the pressure was reduced to 1 micron Hg, no cracking was observed.(5)

The loss of ductility of stressed titanium specimens exposed to hot salt is lessened as the oxygen content or air pressure is reduced.(9,18) This is shown in Figure 8. At an air pressure equivalent to 7[illegible] feet altitude, 34 mm Hg, a decrease in s[illegible]lity is indicated over that at atmospheric [illegible]e for the Ti-8Al-1Mo-1V alloy at 550 F.

Oxygen present in the oxide film may also be sufficient to promote hot-salt cracking.(6,19) For example, two holes were drilled in a Ti-5Al-2.5Sn block. NaCl, C.P. was placed into both holes. TiO_2 was also put into one hole. The holes were closed and welded shut in a vacuum arc furnace. The specimen was rolled at 1800 F and then held at 900 F for 100 hours. No reactivity was observed in the cavity containing NaCl alone, and white crystals remained. The other cavity, however, had reacted to form a black hygroscopic corrosion product.(6)

The necessity for oxygen probably accounts for the fact that cracking occurs at the edges of salt deposits, and is more severe for thin salt coatings.(6,9,17)

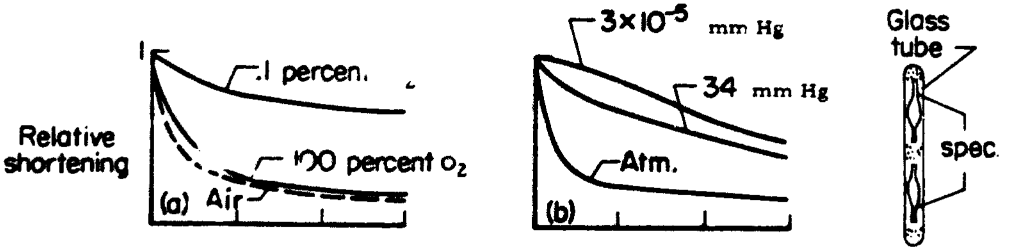
Exposure of salt-coated, bent Ti-8Al-1Mo-1V specimens to 21 mph air flow for 48 hours at 650 F showed no discernable effect of air velocity.(9) Similar specimens, heavily salt-coated, were exposed at 450 F to Mach 3 air for two 25-second runs. Some salt was blown off, but enough remained to cause cracking in subsequent exposure of the self-stressed samples after 95 hours at 600 F in an oven.(9) Further studies are required.

Effect of Water

The role of water in the hot-salt stress-corrosion cracking of titanium alloys is not clearly known. For example, the moisture content of air in the dewpoint range of -40 to 60 F appears to have little effect on the loss of ductility of the Ti-8Al-1Mo-1V alloy at 550 F using NaCl.(9,18) When extra dry oxygen is used in baked out and evacuated equipment, no hot-salt cracking is reported after 2 hours at 800 F with NaCl (<0.01 percent $MgCl_2$).(5) A similar sample with humid air was severely cracked.

In the absence of oxygen, water by itself is not sufficient to promote cracking. For example, when ice was sublimed in an evacuated system free of oxygen, no stress corrosion was found after 2 hours at 800 F.(5)

In other experiments, moisture was reported to exert a strong influence.(19,[illegible]) In one study, the equipment used was nearly closed, and the flow of air could be regulated from an air compressor. Moist air was maintained at 1.8 to 2.8 percent water. Dry air was obtained by passing it at 20 to 40 ml/min through Drierite to give an estimated dewpoint of -100 F(<10 ppm). Cracking of the Ti-8Al-1Mo-1V alloy at 650 F and 50,000 psi stress when exposed to sea salt,(20) required 150 hours



(a) Oxygen.

(b) Air pressure.

FIGURE 8. EFFECT OF OXYGEN AND AIR PRESSURE ON SALT STRESS CORROSION OF DUPLEX ANNEALED Ti-8Al-1Mo-1V ALLOY SHEET AT 550 F(9) (See also Figure 5)

in dry air versus 10 hours for moist air. A similar result was obtained by others.(19)

In experiments using a mixed salt of NaCl and $MgCl_2 \cdot 6H_2O$, severe cracking was reported when using dry oxygen.(15) The water of hydration of the $MgCl_2$ is apparently sufficient to promote the cracking. However, when "a small amount of excess water" is added to the system, longer specimen life was found. This apparently indicates a critical moisture level.

On the basis of these results, it appears that water is a necessary requirement, and must be considered in any mechanism study. When the amount of water present is very low, as with baked-out equipment or dry air, the severity of the test may vary with water content. This could cause the apparent variation in results with different salts in early work. At intermediate water levels, no variation in the severity of attack is noted. At high water levels, the reaction products might be diluted, causing a decline in severity of the attack.

Effect of Chlorine and HCl

Moist chlorine gas was found to cause rapid stress-corrosion cracking of clean, bent Ti-8Al-1Mo-1V specimens at 550 F within 500 hours.(9,18) A dark, purple corrosion product similar in appearance to $TiCl_3$ was formed.

HCl also caused stress-corrosion cracking of polished and stressed samples of Ti-8Al-1Mo-1V at 650 F.(16) Some samples failed within 15 minutes. In one case, no cracks were observed on a specimen after 6 hours. Failure, however, occurred within another half hour. The cracking was intergranular and similar to hot-salt cracks. Electron fractographs indicated fracture was rapid and mechanical. Cleavage of fracture faces was indicated.

Cyclic Exposure

Cyclic exposure to hot salt is apparently less severe even when total time at temperature is the same. Two heats of Ti-8Al-1Mo-1V (duplex annealed) were exposed to alternate dip in 3-1/2 percent NaCl water for 10 minutes and 550 F for 2-1/2 hours at stresses of 50 to 90 percent of yield strength.(8) After 2000 hours (667 cycles) no effects of stress-corrosion cracking were observed, and almost no degradation of physical properties was detected. This can be compared with the 1000-hour degradation as shown in Figure 2.

In other studies, the cycle time and temperature were varied.(9) A salt dip was employed only prior to the exposure. Figure 9 shows the results of this work. Note that the curves indicate time at temperature. Only slight degradation of the ductility of the Ti-8Al-1Mo-1V alloy occurs at 550 F when the cycle time is 2 hours at temperature. The degradation increases as the time at temperature increases. However, even with 16-hour cycle time, the amount of degradation did not appear to be as severe as continuous exposure.

The above studies indicate that an incubation period may be required for stress-corrosion cracking to be initiated. It may be that one of the reactants necessary for cracking is destroyed by the room-temperature exposure. See the section on mechanism for further discussion.

Fatigue

Fatigue does not appear to have much effect on the hot-salt susceptibility of most titanium alloys at elevated temperature.(10) Ti-4Al-3Mo-1V (annealed or aged), Ti-5Al-2.5Sn (annealed), Ti-6Al-4V (annealed or aged), Ti-5Al-2.5Cr-1.25Fe (annealed), and Ti-8Al-1Mo-1V (triplex annealed) were not susceptible to salt-corrosion fatigue at 600 F using synthetic sea salt. The Ti-4Al-3Mo-1V (annealed), Ti-6Al-4V (annealed or aged), and Ti-5Al-2.75Cr-1.25Fe (annealed) were not affected by salt when tested at 800 F. Only Ti-8Al-1Mo-1V showed reduced fatigue life, but only when exposed to synthetic sea salt at 800 F. At 60,000 psi, the cycles to failure were reduced from 10^5 to about 10^4 cycles, at 100 cpm. These results are shown in Figures 10 and 11.

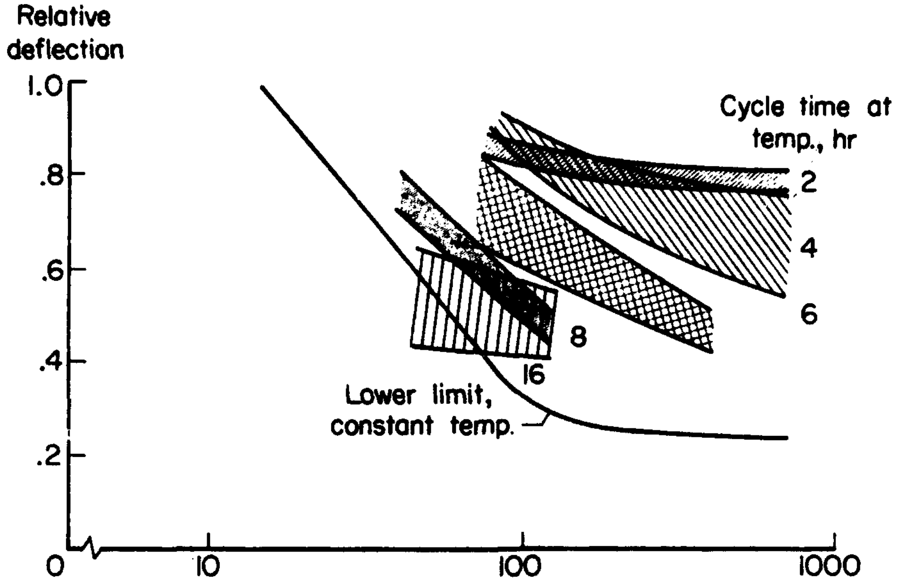
Heat Treatment

The hot-salt stress-corrosion cracking susceptibility of titanium alloys can be altered by heat treatment. For example, Ti-8Al-1Mo-1V is very susceptible in the mill annealed condition, and slightly less in the duplex annealed condition. However, when in the triplex annealed condition, its resistance is much improved, as evidenced by the number of cracks formed on the surface.(17) Thus, at 500 F and 90,000 psi stress after 1000 hours, no cracks (by dye penetration method) were found in the triplex condition while about 10 for the duplex annealed and 1000 for the single annealed condition were found.

The microstructure of alloys also seems to be important. Often, some heats of a particular material are characterized by coarse grain structure.(6) However, even fine grain structure heats were made less resistant by long-term heat treatment at high temperature.(4,6) The grain structure of Ti-6Al-4V was found to change with solution treatment plus aging (24 hours at 1050 F, 1/2 hr 1650 WQ + 8 hr 950 F AC, or 1/2 hr 1700 F WQ + 1/2 hr 1400 F AC). Less beta-phase or more equiaxed structure was observed in the aged material.(6) Long rolling and annealing times were also found to increase the susceptibility of Ti-7Al-12Zr to hot-salt cracking.(6)

Cracking seems to occur both intergranularly and transgranularly although failure was primarily intergranular, in material which was largely alpha-phase.(4)

Heating Ti-6Al-12Zr above its beta-transus (~1825 F) changed the mode of failure from intergranular to transgranular.(6) A similar transition was also found with Ti-5Al-2.5Sn, i.e., heating above 1925 F produced transgranular failure.(6)



Accumulated exposure at 550 F, hr

FIGURE 9. EFFECT OF 2-, 4-, 6-, 8-, and 16-HOUR THERMAL CYCLES ON SALT-STRESS CORROSION OF DUPLEX-ANNEALED Ti-8Al-1Mo-1V ALLOY SHEET AT 550 F

(Tests with residual stress specimens initially bent to 1/8-inch radius for a calculated residual stress of 70 ksi.)(9)

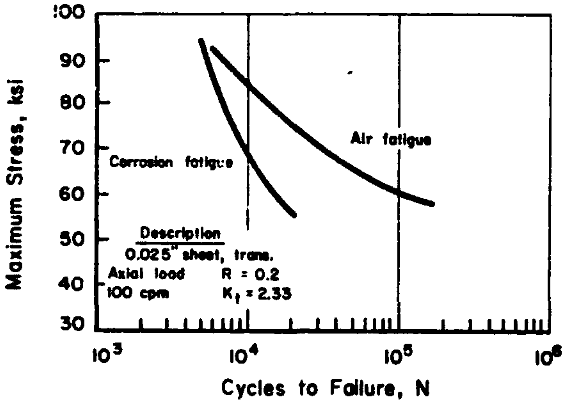


FIGURE 10. CORROSION FATIGUE AND AIR-FATIGUE S-N CURVES FOR Ti-8Al-1Mo-1V TRIPLEX ANNEALED(10)

Tested at 800 F with or without salt coating.

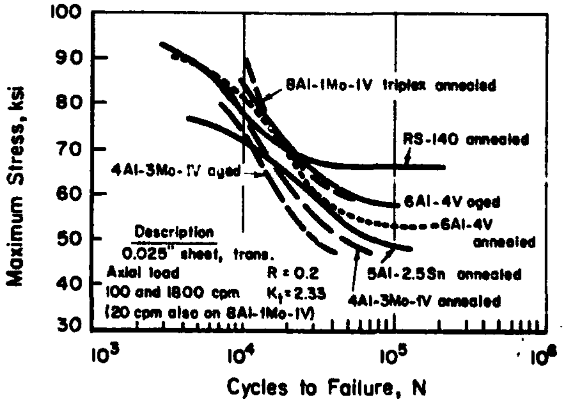


FIGURE 11. CORROSION FATIGUE OR AIR FATIGUE (SAME) S-N CURVES FOR TITANIUM ALLOYS(16)

Tested at 600 F, with and without salt coating.

Segregation of aluminum and vanadium in Ti-6Al-4V and of molybdenum in Ti-8Al-1Mo-1V has been observed in the areas of hot-salt failures.(21) In addition, a distinct change in appearance has been reported in the immediate vicinity of the crack.

Heat treatments at 1450 F, 1650 F, and 1850 F of brake-formed Ti-8Al-1Mo-1V samples apparently provided some resistance to hot-salt cracking at 550 F for short term (30-hour) exposure.(8) However, long term (1000-hour) exposure at 600 F of bent Ti-8Al-1Mo-1V specimens showed only minor improvement when stress relieved in air at 1450 F for 1/2 hour. Stress relief in argon was much more effective than in air.(9)

Surface Treatment and Coatings

No difference was observed between Ti-8Al-1Mo-1V specimens in the as-received or highly polished consition with respect to hot-salt cracking susceptibility.(18)

The use of shot peening and vibratory cleaning apparently increased the resistance of Ti-8Al-1Mo-1V alloys to hot-salt cracking by creating a compressive surface layer.(9,18,22)

The use of certain coatings on a titanium surface shows promise of protection. Surface coatings of nickel plate, aluminum plate and zinc plate show promise of delaying attack, when the coating is non-porous.(6,9,22) In one study, flame-sprayed aluminum and nickel and electroless nickel were porous and not very effective while hot-dipped aluminum gave good protection.(6) In other work at TMCA,(23) promising results were obtained with a duplex nickel coating. This was applied to bar samples of Ti-8Al-1Mo-1V by plating 0.001 in. (0.0005 in. per side) of nickel on a specimen, withdrawing the piece from the bath, rinsing, then activating the piece electrolytically in a proprietary solution (C-12, Puma Corporation). The specimen was then thoroughly rinsed and plated with an additional 0.001 in. of nickel. Several electroplating baths, including Watts B-3, Sulfamate B-28, and Modified Watts-Sulfamate B-39a and b. have been used to apply the duplex coating. Details on the bath compositions and procedures for operating these are given elsewhere. Some test results on the duplex-nickel-coated Ti-8Al-1Mo-1V alloy are given in Table 4.

An organic aromatic polyimide, 1/2 to 1 mil thick, protected Ti-8Al-1Mo-1V from cracking up to 1000 hours at 600 F, before spalling of the coating occurred.(9)

The effect of anodized films on titanium is not completely clear. Gold-anodized (100 to 200 A) and blue-anodized (600 A) films did not prevent the degradation of Ti-8Al-1Mo-1V at 550 F.(18) Specimens of both Ti-8Al-1Mo-1V and Ti-6Al-4V anodized by the aqueous hydrogen phosphate technique were not protected in long term tests.(10,12) In short-term tests, some protection of Ti-8Al-1Mo-1V was obtained by $NaNH_4 \cdot HPO_4$ anodized film.(23) In view of the role of oxygen (even as TiO_2) on the hot-salt cracking, it is not believed that anodized films will offer satisfactory protection.

Postulated Mechanisms

Laboratory studies on the mechanism of hot-salt stress-corrosion cracking of titanium alloys have included such factors as type of salt, effect of oxygen and water, type of reaction (whether solid, liquid, or gaseous), and identification of corrosion products. Studies to date have indicated that several types of chloride salts will initiate failure. However, NaCl now appears to be most reactive.

The role of oxygen and water appears more clear. Oxygen or a reducible oxide (TiO_2) must be present for cracking to occur, although the critical concentration of oxygen is low (1 to 10 microns Hg pressure). Water may also enter into the reaction and appears to be necessary, although its critical concentration is low (on the order of 10 ppm).

Until recently, the type of reaction was believed to be a gas or liquid phase reaction, although failure could not be induced in a specimen separated from the salt by an air gap. This seemed to indicate that a solid phase reaction or a low melting point liquid was required. It was curious, however, that damage around a salt deposit usually flared out above the deposit, indicating a gas phase reaction.(6)

Recent work has indicated that a gas phase reaction can occur.(6) Stressed titanium specimens were placed above, but not touching, (1) NaCl, (2) NaCl + TiO_2, and (3) NaCl + TiO_2 + Ti. After 24 hours at 1200 F or 65 hours at 900 F, cracking was obtained with samples placed above (2) and (3), but not with (1). Also, a U-bend specimen of Ti-6Al-4V stress cracked at 750 F after 20 hours when placed in a tube furnace containing NaCl on Ti chips.

Recently, tentative identification has been made of some of the products of the reaction. X-ray studies have indicated the presence of NaOH,(21) $TiCl_2$,(9,18) and possibly TiO_2(9,15,18,19) and TiO(9,18) in corrosion products. X-ray peaks,

TABLE 4. HOT-SALT STRESS-CORROSION DATA ON NICKEL-COATED Ti-8Al-1Mo-1V ALLOY SPECIMENS(23)

	Salt Exposure				Tensile Properties After Exposure		
Nickel Bath	Temp, F	Time, hr	Stress, ksi	Total Creep Deformation, %	Tensile Strength, ksi	Yield Strength, at 0.2 % Offset, ksi	Elongation, (In./In.) %
Sulfamate B-28	850	150	55	0.49	155	132	18
Ditto	850	150	55	0.75	154	130	20
Modified Watts	850	150	55	0.91	159	134	12
Sulfamate B-39 a and b	850	150	55	1.00	157	133	12
Sulfamate B-28	850	2000	37	0.27	154	132	19
Ditto	850	2000	37	0.39	155	133	21
"	850	2000	37	0.41	154	131	22
"	850	2000	37	0.41	152	133	19
Modified Watts	850	2000	37	0.44	161	140	13
Sulfamate B-39 a and b	850	2000	37	2.22	158	138	8
Ditto	850	2000	37	1.18	160	141	16
"	850	2000	37	0.76	157	138	12

identified as $TiCl_2$, decreased with time. When the corrosion products were dissolved in water, a gas bubbled off and the solution became acidic, as would be expected if $TiCl_2$ were present. The presence of Cl_2 or HCl gas was also indicated when gases from NaCl-Ti mixture at 1200 F were passed through a potassium iodide solution.(6) A gas sample analyzed by a mass spectrograph was found to contain air, water, and chlorine.(6)

On the basis of the above results, the mechanism apparently involves NaCl, O_2, H_2O, and reaction products of $TiCl_2$, NaOH and TiO_2. A possible reaction is:

$$2NaCl + Ti + 1/2O_2 + H_2O = TiCl_2 + 2NaOH.$$
$$(\Delta F \; -40 \text{ Kcal at } 600 \text{ K})$$

That an unstable intermediate such as $TiCl_2$ is involved, is further indicated by the cyclic studies (room temperature to operating temperature) in which reduced susceptibility is found.

Studies have shown that aluminum and vanadium may be selectively attacked, since their concentrations are relatively higher in the corrosion products.(16) NaOH by itself will also give selective attack, but no cracking. Inhibition of stress cracking was obtained by a pretreatment in NaOH at 650 F for 7 days before salt exposure.

A more recent theory proposes that NaCl and water react to form NaOH and HCl.(16) The HCl reacts with the protective oxides on the surface, forming unprotective chlorides. The hydrogen released by the attack of the exposed titanium is then believed to diffuse into the metal to cause subsequent hydrogen embrittlement.

This mechanism does not entirely account for the apparent need for oxygen, but indicates the need for water. The HCl detected in this work(16) might come from decomposition of $TiCl_2$ with water, as suggested in Reference 5.

STRESS-CORROSION CRACKING BY SILVER AND SILVER COMPOUNDS

At high temperature, silver, silver chloride, and silver braze have been shown to have a definite, detrimental effect on titanium alloys, and appear to cause a form of stress-corrosion cracking.

A silver braze coating (Dynabraze "B", consisting nominally of 94.8Ag-5Al-0.2Mn) on titanium alloys Ti-8Al-1Mo-1V and Ti-6Al-4V caused rapid surface deterioration, loss of adhesion between braze and metal, and stress-corrosion cracking after exposure in air at 650 F.(21) (See Table 2.) Of the failed titanium specimens, only slight differences in failure time were noted between brazed specimens with or without salt and in the notched or unnotched condition. For the Ti-6Al-4V alloy, notched specimens were stressed to 45 or 58 ksi and unnotched specimens to 23 to 37 ksi. Failure times ranged from 5500 to 15, 000 hr. For the Ti-8Al-1Mo-1V alloy, notched specimen stress was 56 to 67 ksi and unnotched specimen stress was 23 to 31 ksi. Failures occurred after 9000 to 18,500 hr.

An investigation of failure of a titanium alloy engine compressor wheel operated at high temperature showed the role of silver and silver chloride in stress-corrosion cracking of titanium alloys.(24) Previous compressor tests below 700 F showed no failures. Tensile specimens of Ti-7Al-4Mo and Ti-5Al-2.5Sn, uncoated and coated with silver chloride, silver plate, vacuum deposited silver, and/or F50 hydraulic oil and salt were used. The results are shown in Table 5. Both silver and silver chloride caused stress-corrosion failure of the alloys at 700 F and higher. No reduction of room-temperature properties was found after short-term exposures of Ti-7Al-4Mo at 600 F. As a result of this work, the use of silver plating these parts was discontinued. Instead, organic bonded dry film lubricants or graphite greases were adopted in place of silver thread lubricants and molybdenum disulfide was selected over silver anti-fretting agents.

Before other silver compounds are applied to titanium, a complete evaluation of the effects of stress and temperature on the stress-corrosion cracking by silver is recommended.

STRESS-CORROSION CRACKING BY CADMIUM

In the period of 1956-1957, experiences confirmed that both the Ti-4Al-4Mn and Ti-8Mn alloys were susceptible to stress-corrosion cracking by molten cadmium, i.e., at temperatures above about 610 F. Details of these experiences have been summarized in an earlier DMIC report.(1) In general, it is believed that for attack to occur:

1. Fissures must exist in the TiO_2 surface so that unprotected titanium will be exposed.
2. The temperature must be high enough to permit the cadmium to flow into the fissures.

However, no stress-corrosion cracking is anticipated when using cadmium in contact with titanium below 610 F.

STRESS-CORROSION CRACKING IN RED FUMING NITRIC ACID

Titanium has low corrosion rates in both white and red fuming nitric acid.* See References 25 and 26. However, titanium suffers severe stress-corrosion cracking and/or pyrophoric reaction in dry red fuming nitric acid. Water addition of 1.5 to 2 percent inhibits this reaction. The current military specification of 2.5 ± 0.5 percent water in red fuming nitric acid is safe for use with titanium. The 0.6 percent addition of HF added to inhibit attack of stainless steels and aluminum increases the corrosion attack of fuming nitric acids on titanium.

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* Military Specification:

White fuming HNO_3 - 97% Min HNO_3, 0-.015 % NO_2, 2% Max H_2O

Red fuming HNO_3 - 82-85% HNO_3, 14 ± 1% NO_2, 2.5 ± 0.5% H_2O.

TABLE 5. RESULTS OF STRESS-CORROSION STUDIES OF TITANIUM ALLOYS WITH SILVER AND SILVER CHLORIDE(24)

Temperature, F	Stress, ksi	Coating	Failure Time, hours
		Ti-7Al-4Mo	
800	100	Bare	40-396
800	100	NaCl	1.4-2.6
800	50	NaCl	NF(a) 260(b)
800	50(c)	NaCl	NF(a) 260(b)
800	25	NaCl	NF 260
800	100	AgCl	0, 0.06
600	110	Bare	NF 110(d)
600	110	AgCl	NF 110(d)
875	70	Bare	146, 182
875	70	F50(e)	NF 112
875	70	Ag plate	18.5
875	70	Ag plate + F50(e)	20
875	70	Ag plate + NaCl	4.8
875	70	Ag plated and then stripped	120
875	70	Ag (Vac. Dep.)	8, 9
875	70	Ag plated bolt (NaCl coated and washed)	33
875	70	Ag plated bolt from service	41
875	70	Ag plated bolt	26
		Ti-5Al-2.5Sn	
900	48	Bare	NF 100
900	48	AgCl	0.03, 0.06
800	58	Bare	NF 100
800	58	AgCl	0.8
700	64	Bare	NF 100
700	64	AgCl	19.5
500	71	Bare	NF 100
500	71	AgCl	145
875	50	Bare	175, 447
875	50	F50(e)	394, 659
875	50	Ag plate	0.4, 0.6
875	50	Ag plate + F50(e)	0.3, 1.8
875	50	Bare	184, 304
875	50	NaCl	36, 40
875	50	Ag (vacuum deposit)	15
875	50	Ag (vacuum deposit) + NaCl	1.3
875	50	Au (vacuum deposit)	156, 241
875	50	Au (vacuum deposit) + NaCl	1.5
875	50	Ni (vacuum deposit)	210
875	50	Ni (vacuum deposit) + NaCl	23
875	50	Ag plated bolt	117

(a) NF means no failure.

(b) Severely cracked.

(c) Notched specimen.

(d) Room-temperature properties after test; yield 150-153 ksi, El 10-11 percent.

(e) Hydraulic oil.

STRESS CORROSION IN METHYL ALCOHOL SOLUTIONS

Titanium (as well as zirconium) has been found to suffer stress-corrosion cracking in methanol containing HCl or H_2SO_4.(27) U-bend specimens were exposed to various concentrations of HCl or H_2SO_4 in methanol. Cracking of titanium occurred within about an hour in methanol with 0.4 percent HCl, and in about a day with 1 percent H_2SO_4. The cracking time decreased with increasing concentration of HCl. A concentration as low as 0.005 percent caused cracking within 24 hours. The cracking time decreased as the solution temperature was raised.

The presence of water in the methanol-0.4 percent HCl solution increases the time required for failure. With an addition of 1.5 percent water, no failure of titanium was observed.

When the titanium U-bend specimens were annealed at 930 F for 10 minutes or at 840 F for 1 hour, no stress-corrosion cracking was then found in the HCl solution.(27)

Studies have shown that solutions of methyl alcohol with additions of bromine are extremely corrosive to titanium and titanium alloys.(28) Corrosion data are presented in Table 6. Severe intergranular attack of titanium was also observed in the dilute bromine solution. As a measure of the susceptibility to localized attack, a "tendency" to intergranular attack was calculated as the increase in ohmic resistance divided by the weight loss of the specimen. As shown in Table 6, unalloyed titanium has a high tendency to intergranular attack in 1 percent bromine. This tendency decreases with higher bromine content, as the corrosion rate increases.

TABLE 6. CORROSION OF SEVERAL RUSSIAN ALLOYS IN METHYL ALCOHOL-BROMINE SOLUTIONS(28)

Alloy(1)	Corrosion, mpy, for Bromine Content indicated, percent				
	1	2	3	4	5
VT1 (Unalloyed grade)	180	290	480	650	810
VT5 (5Al)	130	220	320	410	530
VT3 (4.7Al-2.5Cr)	70	140	210	280	360
VT3-1 (4.4Al-2Cr-1Mo)	65	120	140	190	-
Iodide titanium	70	140	180	240	290
Intergranular Attack, Tendency(2)					
VT1	19	11	5	4	3

(1) *Iodide, VT1 and VT5 are alpha alloys. VT3 and* VT3-1 are alpha-beta alloys.

(2) See text.

The corrosion rate of titanium is substantially lowered by additions of water to methyl alcohol-bromine solutions. See Table 7. With the first additions of water, the severity of intergranular attack increases, and reaches a maximum at 5 percent water. This tendency to localized attack then decreases with further water additions and becomes nil at 30 percent water.

The attack of titanium in methyl alcohol-bromine solutions is electrochemical in nature. Protection of titanium in water-free solutions can be accomplished by cathodic polarization to about 0.350 volt.

TABLE 7. EFFECT OF WATER ON CORROSION OF VT-1 UNALLOYED TITANIUM IN METHYL ALCOHOL-2 PERCENT BROMINE SOLUTIONS(28)

Water, percent	0	2.5	5	10	20	30
Corrosion, mils per year	290	250	210	80	50	Nil
Intergranular Attack, tendency(1)	11	28	55	17	5	Nil

(1) See text.

STRESS-CORROSION CRACKING IN NITROGEN TETROXIDE

Mounting unpublished evidence has been accumulated since the summer of 1965 which indicates that the Ti-6Al-4V alloy is susceptible to stress-corrosion cracking in liquid N_2O_4. While much of information is still tentative, it has been shown that failures can occur in solution-treated and annealed Ti-6Al-4V sheet at stresses and temperatures as low as 90,000 psi and 105 F in times as short as 40 hours. The various parameters which may enter into this reaction (e.g., N_2O_4 purity, alloy condition, temperature, stress level, time, etc.) are now under intensive evaluation in several coordinated programs being monitored by Bell Aerosystems for NASA. It is anticipated that a preliminary summary of the findings from these investigations will be released for dissemination by DMIC in the near future.

STRESS-CORROSION CRACKING IN MERCURY

A 1962 reference(29) reported that the Ti-13V-11Cr-3Al beta alloy suffered unusually severe cracking attack in both the liquid and vapor phase of mercury at 700 F. Also, embrittlement of titanium scrap and alloys Ti-75A and Ti-6Al-4V has been observed when titanium was deformed while immersed in mercury.(30) Wetting of unstressed titanium by mercury requires a temperature of 750 F in vacuum, while reexposure to air causes dewetting.(30) These reports indicate that stress-corrosion cracking of titanium and its alloys can occur in mercury. Consequently, additional studies in this area are recommended before committing titanium or its alloys to use in contact with mercury.

ACCELERATED CRACK PROPAGATION OF PRECRACKED MATERIALS

Recent studies have shown that many materials including titanium alloys have a susceptibility to stress-corrosion cracking in environments in which susceptibility was not previously known. These studies use special techniques which reduce the time-to-failure of a conventional stress-corrosion cracking specimen. These techniques employ precracked specimens and are about the same as those used currently on high-strength alloys for the determination of fracture-toughness(31) and delayed failure.(32) Thus, calculations for fracture toughness are made which assume conditions of plane strain. Susceptibility to cracking is then measured by comparing the stress intensity factor, K, in psi √in., obtained in air with the K value obtained in the liquid media. In environments in which stress-corrosion cracking is a factor, the fatigue crack propagates to produce rapid failure.

The accelerated crack-propagation technique differs from ordinary stress-corrosion cracking evaluations in that by the use of a notch or crack the incubation period is essentially eliminated.

Experimental Techniques

The basis of these techniques lies with the use of a fatigue-cracked specimen in which a stress riser already exists and to which a stress and a selected environment are applied. The specimens are prepared by sawing or machining a notch into one edge or the center of the sample and then fatiguing the specimen so that a crack is initiated to give a total crack length (including the notch depth) of 20 to 30 percent of the specimen width. This fatigue crack thus acts as a stress riser in the specimen in much the same manner as a pit, or other natural stress concentrator that results from corrosion of the specimen.

Stress can be applied to the specimen either by tensile loading, multiple-point bending or cantilever loading. A plastic container placed around the specimen contains the environment, or the test medium is dripped onto the cracked area. The specimen is loaded to a given value and the time to failure noted. An alternate method is to step-load the specimen to a higher load level if failure does not occur within a fixed time. Additional details of this procedure are given in References 3 and 33.

When precracked titanium specimens are loaded rapidly in an environment such as dry air, failure usually occurs by plane strain at high stresses. This point is sometimes used as a reference point to compare with stress-corrosion cracking failures (see Figure 12). However, if longer times at constant load are used, failure will occur at lower values in air as shown in Figure 12. True base-line data in vacuum are not presently available. When an environment such as salt water is used, the fatigue crack may propagate at lower stresses, causing failure at reduced stress values as shown in Figure 12.

The appearance of failed specimens is shown in Figure 13. The initial fatigue crack is the fan-shaped crack at the bottom. In air, failure occurs by plane strain and is often marked by shear lips. In sea or salt water, the crack propagates slowly by a stress-corrosion cracking mechanism, as shown by the area in the center of the specimen. This has a brittle appearance usually associated with stress-corrosion cracking. When the specimen will no longer withstand the stress, rapid failure occurs by plane strain.

The degree of susceptibility of a material to stress-corrosion cracking is measured by comparing its air failure stress intensity factor, K, in ksi $\sqrt{\text{in.}}$ to its value in salt water as shown in Figure 14. The stress intensity factor for stress-corrosion cracking, $K_{I_{scc}}$, is that value above which failure occurs as illustrated in Figure 14. Note that this value is essentially reached after a short time and that this time period can vary from one material to another.

Salt Water

Most of the current research on stress-corrosion cracking of titanium alloys employs salt water or seawater. This emphasis is due to the current consideration of titanium for service in undersea vehicles and structures and for aircraft operating in seacoast atmospheres.

Susceptible Alloys

Alloys which have shown some degree of susceptibility are listed below but not necessarily in order of susceptibility:

Unalloyed Ti (with high oxygen content, i.e., 0.317 percent)
Ti-8Mn
Ti-2.5Al-1Mo-10Sn-5Zr (IMI-679)
Ti-3Al-11Cr-13V
Ti-4Al-4Mn
Ti-5Al-2.5Sn
Ti-6Al-2.5Sn
Ti-6Al-4V
Ti-6Al-3Cb-2Sn
Ti-6Al-4V-1Sn
Ti-6Al-4V-2Co
Ti-6Al-6V-2.5Sn
Ti-7Al-2Cb-1Ta
Ti-7Al-3Cb (as received and beta annealed)
Ti-7Al-3Mo
Ti-7Al-3Cb-2Sn
Ti-8Al-1Mo-1V
Ti-8Al-3Cb-2Sn

Preliminary screening tests indicate the following alloys to be insensitive to seawater crack propagation for the condition used:

Ti-2Al-4Mo-4Zr
Ti-4Al-3Mo-1V
Ti-5Al-2Sn-2Mo-2V
Ti-6Al-2Mo
Ti-6Al-2Sn-1Mo-1V
Ti-6Al-2Sn-1Mo-3V
Ti-6Al-2Cb-1Ta-0.8Mo
Ti-6.5Al-5Zr-1V
Ti-7Al-2.5Mo (as received and beta annealed + WQ + 110 F - aged for 2 hr)

Table 8 presents some approximate values of the stress-intensity threshold factor, $K_{I_{scc}}$, for several susceptible alloys. Each value was obtained from constant loading to failure of 2 to 6 specimens. Note that considerable variation is evident in $K_{I_{scc}}$ in different conditions of the same alloy. Heat treatment, composition, and size of specimen can also affect the results (see discussion in later sections).

Table 9 presents results from a study using precracked Charpy specimens.(37) A constant load was applied by 3-point beam loading. The data in Table 9 also show different susceptibilities between heat treatments for a given alloy. Some heat treatments of Ti-6Al-4V, Ti-7Al-2Cb-1Ta, and Ti-3Al-11Cr-13V show low susceptibility. Ti-75A does not appear to be susceptible. Ti-4Al-4Mn has poor fracture toughness but does not seem to be susceptible to cracking in the condition shown. Table 10 shows representative values for two aluminum alloys which do not show susceptibility.

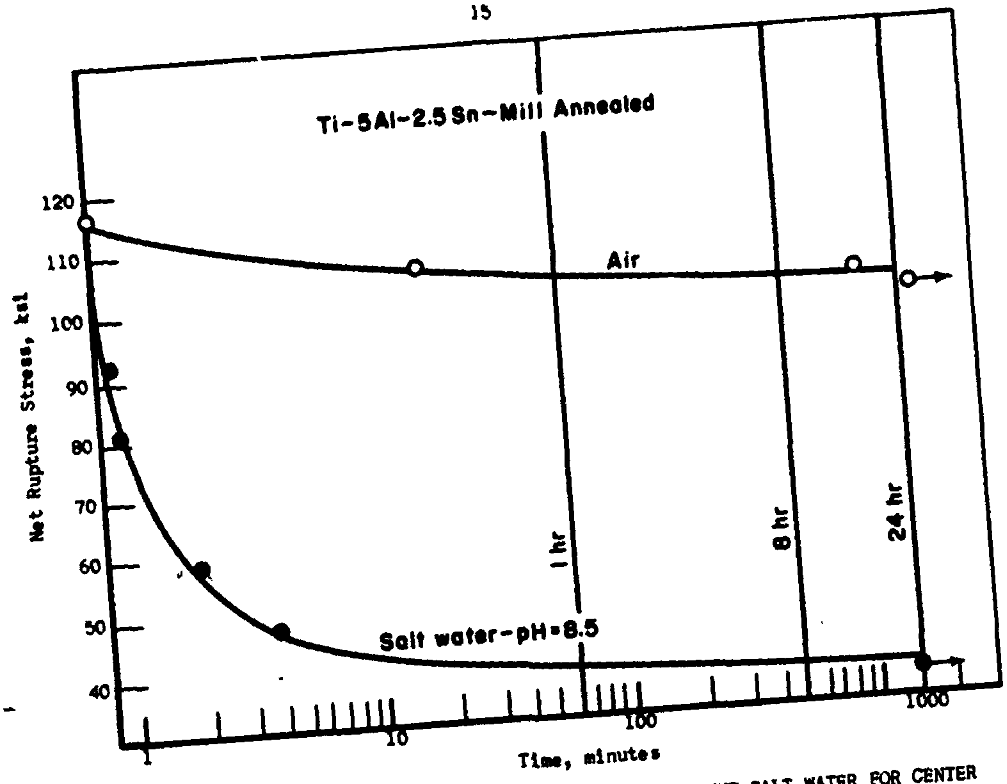

FIGURE 12. STRESS-RUPTURE CURVES IN AIR AND 3.5 PERCENT SALT WATER FOR CENTER FATIGUE-CRACKED SPECIMENS(34)

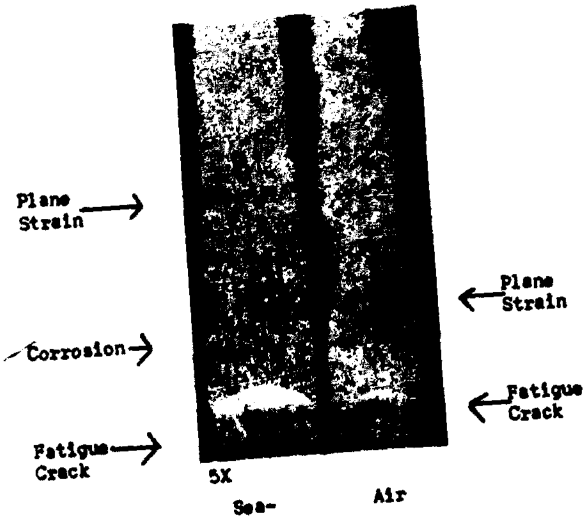

FIGURE 13. APPEARANCE OF FAILED NOTCH-TEST SPECIMENS, MATERIAL USED WAS 0.125-IN-THICK SHEET OF Ti-5Al-2.5Sn ALLOY(35)

The photograph was reduced approximately 20 percent in printing.

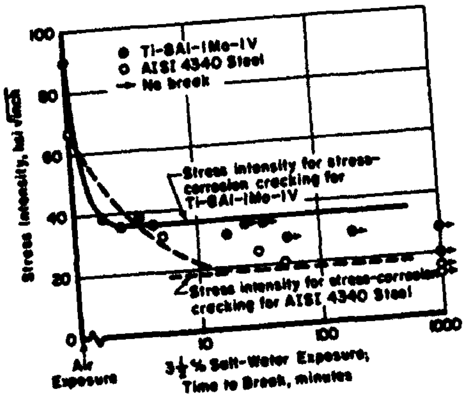

FIGURE 14. TEST RESULTS FOR Ti-8Al-1Mo-1V AND AISI 4340 STEEL IN AIR AND AQUEOUS 3.5% NaCl ENVIRONMENT(3)

Fatigue precracked cantilever-beam specimens.

TABLE 8. APPROXIMATE STRESS INTENSITY THRESHOLD VALUES FOR TITANIUM ALLOYS SUSCEPTIBLE TO STRESS-CORROSION CRACKING IN 3-1/2% SALT WATER(36)

Alloy	Condition	Specimen Cross Section,(1) in.	Yield Strength, ksi	Stress Intensity For Instantaneous Air Failure, ksi $\sqrt{in.}$	Stress Intensity For Stress-Corrosion Cracking, K_{Iscc}, ksi $\sqrt{in.}$
Ti-7Al-2Cb-1Ta	As Received	1 x 11/16	102	100-115	40
		1 x 1/2		100-110	63
Ti-7Al-2Cb-1Ta	As Received	7/8 x 1/2	105-110	100	35
Ti-7Al-2Cb-1Ta	As Received	1 x 11/16	106	105	43
Ti-7Al-2Cb-1Ta	As Received	1/2 x 1/2	113	40	40
Ti-7Al-2Cb-1Ta	As Received	1 x 1/2 (2)	131	130	88
Ti-8Al-1Mo-1V	1825 F/1 hr/AC	1 x 1/2	108	110	28
Ti-8Al-1Mo-1V	1700 F/1 hr/AC + 1200 F/2hr/WQ	1 x 1/2	120	90	23
Ti-8Al-1Mo-1V	As Received	1/8 sheet	130	55	18
Ti-6Al-4V	As Received	1 x 11/16(3)	118	90	67
Ti-6Al-4V	As Received	1/2 x 1/2	124	115	95
Ti-6Al-4V	As Received	3/4 x 1/10	165	65	55
Ti-5Al-2.5Sn	As Received	1 plate	113	130	72
Ti-5Al-2.5Sn	As Received	1/2 x 1/2	114	110	39
Ti-6Al-4V-1Sn	1825 F/1 hr/WQ + 1100 F/2 hr/ AC	1 x 11/16(3)	131	115	42
Ti-6Al-6V-2.5Sn	1550 F/1 hr/WQ + 900 F/4 hr/ AC	1 x 3/4	183	55	21
Ti-6Al-2Mo	1750 F/1 hr/AC + 1100 F/2 hr/ WQ	1/2 x 1/2	124	115	76
Ti-6Al-2Mo	Same as above	1 x 11/15(3)	125	120	102
Ti-7Al-3Mo	As Received	1 plate	107	130	45
A-70(4)	As Received	1/2 x 1/4	80	65	44

(1) Specimen cracked through longest dimension.

(2) Side grooved to 3/8 inch.

(3) Side grooved to 1/2 inch.

(4) High interstitials.

TABLE 9. APPROXIMATE STRESS INTENSITY VALUES FOR TITANIUM ALLOYS BY CHARPY SPECIMENS IN LIQUID ENVIRONMENT(1)

Alloy	Condition	Plate Thick, Inches	Grain Direction	Apparent Fracture Toughness Parameter K_{Ii}, ksi √in. Air(2)	Air	3-1/2 % NaCl
Ti-8Al-1Mo-1V	Duplex Anneal	2.5	T	68	55	28(3)
Ti-8Al-1Mo-1V	Duplex Anneal	0.5	L	48	46+	35
Ti-8Al-1Mo-1V	Mill Anneal	0.5	L	49	41+	27
Ti-8Al-1Mo-1V	Hot Roll above β transus	0.5	T	48		25
Ti-8Al-1Mo-1V	1450 F/1 hr/AC + 1100 F/8 hr/AC	0.5	L	48	41+	28(4)
Ti-8Al-1Mo-1V	1450 F/1 hr/WQ + 1100 F/8 hr/AC	0.5	L	48		32(4)
Ti-8Al-1Mo-1V	1650 F/1 hr/AC + 1100 F/8 hr/AC	0.5	L	97	43	27
Ti-8Al-1Mo-1V	1650 F/1 hr/WQ + 1100 F/8 hr/AC	0.5	L	45	41	26
Ti-8Al-1Mo-1V	1850 F/1 hr/AC + 1100 F/8 hr/AC	0.5	L	55	51	31
Ti-8Al-1Mo-1V	1850 F/1 hr/WQ + 1100 F/8 hr/AC	0.5	L	37		24(5)
Ti-6Al-4V	Mill Annealed	0.5	T	45		37
Ti-6Al-4V	Mill Annealed	0.5	T	59	51	41(6)
Ti-6Al-4V	1725 F/1/2 hr/WQ + 1250 F/4 hr/AC	0.5	T	59		53
Ti-6Al-4V	1550 F/1/2 hr/WQ + 1250 F/4 hr/AC	0.5	T	52		50
Ti-6Al-4V	1850/1/2 hr/WQ	0.5	T	58	55	56
Ti-6Al-4V	1550 F/6 hr/WQ	0.5	T	68	69	67
Ti-6Al-4V-2Co	1600 F/2 hr/AC	0.5	T	65	55	32
Ti-7Al-2Cb-1Ta	1650 F/1 hr/WQ	0.5	T	84		73
Ti-7Al-2Cb-1Ta	1650 F/1 hr/WQ + 1300 F/1/2 hr/AC	0.5	T	83		48
Ti-4Al-4Mn	Heat Treated(7)	0.375	T	22	15	14
Ti-6Al-6V-2Sn	1300 F/2 hr/AC	-	T	44		33
Ti-6Al	1550 F/2 hr/AC	0.5(8)	L	84		29
Ti-3Al-11Cr-13V	1425 F/1/2 hr/WQ	0.12(9)	T	55	45	41
Ti-3Al-11Cr-13V	1425 F/1/2 hr/WQ + 1300 F/1/2 hr/AC	0.12(9)	T	88		28
Ti-75A	1300 F/2 hr/AC	0.1(9)	T	69	51	61
Ti-75A	1550 F/1/2 hr/WQ	0.1(9)	T	64	58	62

(1) Cross-section 0.394 x plate thickness, specimen cracked through 0.394 dimension.
(2) Loaded to failure.
(3) K_{Ii} in water is 32; 50% HNO_3, 32; 2% HF, 30 ksi √in.
(4) K_{Ii} in kerosene is 41 ksi √in.
(5) K_{Ii} in kerosene is 31 ksi √in.
(6) K_{Ii} in tap water is 57 ksi √in.
(7) Estimated yield strength - 140,000 psi.
(8) Rod.
(9) Sheet.

TABLE 10. APPROXIMATE STRESS INTENSITY VALUES FOR OTHER ALLOYS BY CHARPY SPECIMENS(a) IN LIQUID ENVIRONMENT(37)

Alloy	Condition	Plate Thickness, Inches	Grain Direction	Parameter K_{Ii}, ksi √in. Air	3-1/2% NaCl
Al 2024	T 351	0.5	T	31	28+
Al 7075	T 651	0.5	T	23	22+

(a) Cross section 0.394 x plate thickness. Specimen cracked through 0.394 dimension.

(b) Loaded to failure.

Preliminary data as shown in Tables 11 and 12 indicate the unalloyed titanium with high oxygen, as well as several alpha and near-alpha alloys, are susceptible. These data compare nominal bending stresses at failure in air with failure in seawater. All specimens that failed in seawater had a typical appearance of brittle fracture. Several non-susceptible alloys are also shown.

The susceptibility of pre-cracked titanium alloys to stress-corrosion cracking in salt water appears to be affected by the aluminum and tin content and isomorphous beta stabilizers.(38,39) Data compiled in Table 11(38) indicate that the susceptibility occurs with higher aluminum or aluminum-tin contents. A notable exception to this general trend is the susceptibility of the Ti-8Mn alloy.

In the system Ti-6Al-2Cb-1Ta, almost no susceptibility was found for alloys with an aluminum content of 6 percent, while sensitivity was found at aluminum levels of 6.5 and 7 percent(39) (see Figure 15). Ti-6Al-3Cb is almost completely resistant to cracking, while Ti-7Al-3Cb and Ti-6Al-3Cb-2Sn were sensitive.(38) Ti-6Al-2Cb-1Ta alloy was less sensitive than Ti-7Al-2Cb-1Ta, which agrees with Figure 15.

The presence of isomorphous beta-stabilizers - molybdenum, vanadium, and columbium - tends to reduce the sensitivity of titanium alloys. Titanium alloys containing 5 to 7 percent aluminum plus 1 to 4 percent vanadium and/or molybdenum were found to be insensitive. The addition of molybdenum to Ti-7Al-2Cb-1Ta or Ti-7Al-3Cb tended to reduce their susceptibility to cracking,(38,39) as shown in Figure 16. The addition of molybdenum is currently being considered as a compositional improvement for certain alloys, in order to reduce their cracking potential in salt water. For example, the Navy is currently testing a Ti-6Al-2Cb-1Ta-0.8Mo modification of the Ti-7Al-2Cb-1Ta alloy.

Effect of Heat Treatment

The degree of susceptibility of some titanium alloys to stress-corrosion cracking can be changed by the heat treatment given the material. The cooling rate from temperatures above the beta transus and the times and temperature of aging in the 900 to 1300 F range are among the factors which have been identified as important.(37,38,39)

Ti-Al-Cb System. The titanium system Ti-7Al-3Cb, with and without molybdenum, was found to be completely free from stress-cracking when water-quenched after an anneal of 1 hour at 1950 F. Air cooling from this temperature, however, resulted in susceptibility. Also, quenching of Ti-7Al-2Cb-1Ta from above the beta transus resulted in improved resistance for this susceptible alloy.(38) See Table 13.

An aging treatment at 1100 F for 2 hours resulted in renewed sensitivity of the Ti-7Al-3Cb and Ti-7Al-3Cb-0.2Mo alloys. With an increase of molybdenum to Ti-7Al-3Cb-0.8Mo, complete resistance to cracking in salt water was obtained when the alloy was water-quenched or air-cooled, but not when it was furnace-cooled. The air-cooled alloy was made sensitive when it was heated 2 hours at 1100 F.(38) (See Table 13.) Thus, to obtain resistance to cracking for susceptible alloys of the Ti-Al-Cb system, it is apparent that heat-treatment modifications may be as important as composition changes.

Ti-8Al-1Mo-1V. Table 14 and Figure 17, present the results of a similar study to explore the relationship between time and temperature on the susceptibility of the Ti-8Al-1Mo-1V alloy.(39) The results show that the susceptibility is decreased and eventually eliminated when the annealing temperature is increased. The lowest temperatures for no susceptibility were 1800 F for the air-cooled condition and 1550 F for the water-quenched condition. As shown earlier by the data of Table 9, this alloy is quite susceptible in the mill-annealed and duplex-annealed conditions. However, the triplex-anneal heat treatment was found to give good resistance to salt-water cracking for 0.8 inch plate, provided a short (15 minute) anneal at 1375 F followed by air cooling was used, with no subsequent heating in this temperature range.(39)

Ti-6Al-4V. Mill annealed Ti-6Al-4V is susceptible to salt-water cracking, but proper heat treatment can reduce or eliminate this susceptibility.(37,39) Table 15 shows the effect of annealing temperatures and cooling rates for Ti-6Al-4V. The susceptibility was determined by the appearance of the fracture face. Annealing temperatures above 1700 F with an air cool or above 1550 F with a water quench resulted in no appearance of cracking in seawater for 0.75-inch plate.

Since Ti-6Al-4V is a mildly beta-stabilized alloy, heat treatment above 1400 F with air cooling could result in metallurgical instability in service. Therefore, a duplex anneal was investigated.(39) This anneal consists of heating 1700 F to 1850 F for 1 hour and air cooling (AC) followed by a low-temperature stabilizing treatment (1200 to 1500 F for 1/2 hour, AC). This treatment is reported to result in an over-all improvement in fracture toughness, with only slight sensitivity to salt-water cracking.(39) See Table 16.

Effects of Ordering and Microstructure. The susceptibility of high aluminum-bearing titanium alloys to salt-water cracking is believed to be due to ordering of the microstructure.(38,39) This ordering is believed to be the result of the formation of Ti_3Al. It has previously been shown that 6 to 10 percent aluminum in titanium can cause embrittlement by ordering when the binary alloy is aged in the 900 to 1300 F region.(40) This coincides perfectly with the stress-corrosion cracking susceptibility found for certain high aluminum-bearing titanium alloys heat treated in this temperature range.

A correlation is believed to exist between microstructure and seawater cracking for several aluminum-bearing titanium alloys.(38) In these experiments, materials with a matrix of coarse, long platelets in the microstructure were the most susceptible. Materials with fine platelets and alpha dispersions were not susceptible. Normally, susceptible material was improved by water-quenching from a high temperature beta-anneal.

TABLE 4. EFFECT OF SEAWATER ON TITANIUM ALLOYS[1](38)

Titanium Alloy	Condition	Nominal Bending Stress in Air			Nominal Bending Stress in Seawater		
					Static-Load Cantilever Test		
		Slow-Notch Bend Test	Static-Load Cantilever Test				
		Sn ksi	Sn ksi	Time min	Sn ksi	Time min	Fracture Appearance Sea-Water Embrittled?
Alpha Alloys							
Ti Unalloyed (RS-70)	Alpha Rolled	182	157	45	64	3	Yes
	Alpha Rolled + 1400 F, 16-Hr AC	-			104	1	Yes
5Al-2.5Sn	Alpha-Beta Rolled	170			65	3	Yes
6Al-2.5Sn	Beta Rolled	233	181	40	110	3	Yes
	Alpha-Beta Rolled	221	166	760	109	6	Yes
Near-Alpha Alloys							
8Al-2Cb-1Ta	Beta Rolled	186			129	Immed	Yes
7Al-3Cb (0.06 O_2)	Beta Rolled	232			110	10	Yes
	Alpha-Beta Rolled	193	166	70	125	3	Yes
7Al-3Cb (0.1 O_2)	Beta Rolled	235			144	Immed	Yes
	Alpha-Beta Rolled	256			131	4	Yes
7Al-3Cb-2.5Sn	Beta Rolled	200			111	1	Yes
	Alpha-Beta Rolled	213			114	9	Yes
6Al-3Cb-2Sn	Beta Rolled	220			120	Immed	Yes
7Al-3Cb-2Sn	Beta Rolled	233			158	Immed	Yes
8Al-3Cb-2Sn	Beta Rolled	110			126	Immed	Yes
6.5Al-5Zr-1V	Alpha-Beta Rolled	222	186	180	186	200	No
Alpha-Beta Alloys							
6Al-2Sn-1Mo-1V	Alpha-Beta Rolled	209	196	9	180	1430	No
6Al-4V (Low O_2)	Alpha-Beta Rolled				180	Immed	No
6Al-4V (High O_2)	Alpha-Beta Rolled	101	135	15	103	150	No
6Al-2Mo	Alpha-Beta Rolled				165	180	No
	Alpha-Beta Rolled + 1750 F, 1-Hr AC + 1100 F, 2-Hr AC				191	1	No
7Al-2.5Mo	Alpha-Beta Rolled	209	198	500	169	Immed	No
	Alpha-Beta Rolled + 1735 F, 1-Hr WQ	216			192	150	No
	Alpha-Beta Rolled + 1735 F, 1-Hr WQ + 1100 F, 2-Hr AC	205	166	25	135	13	No
5Al-2Sn-2Mo-1V	Beta Rolled	242	190	6	177	105	No
	Alpha-Beta Rolled	185	171	1	143	110	No
6Al-2Sn-3V-1Mo	Beta Rolled	211	115	1845	120	342	No
	Alpha-Beta Rolled	192	106	1780	140	2	No

[1] All specimens were fatigue cracked to a total notch depth of 25 to 35 percent.

Immed - Immediate

TABLE 12. FRACTURE STRESS OF SEVERAL TITANIUM-BASE ALLOYS IN AIR AND SEAWATER(39)

Alloy	Heat Treated Condition	Specimen Size, in.	Fracture Stress At Crack Root, ksi Air	Fracture Stress At Crack Root, ksi Sea Water	Percent of Air Stress	Fracture Surface Appearance
Ti-5Al-2.5Sn (Normal)	1450 F-1 Hr-AC	0.754	287	192	67.0	Definite corrosion
Ti-5Al-2.5Sn (ELI)	1450 F-1 Hr-AC	0.786	320	141	44.1	Definite corrosion
Ti-4Al-3Mo-1V	1350 F-2 Hr-FC	0.930	257	179	69.6	No corrosion - rough fracture in both air and seawater
Ti-4Al-3Mo-1V	1650 F-1 Hr-WQ; 950 F-8 Hr-AC	0.932	158	144	91.2	No corrosion - rough fracture in both air and seawater
Ti-13V-11Cr-3Al	1450 F-1 Hr-AC	0.980	264	139	52.6	Definite corrosion
Ti-13V-11Cr-3Al	1450 F-1 Hr-WQ; 900 F-40 Hr-AC	0.994	89	95	107.0	No corrosion
IMI-679	1650 F-1 Hr-AC; 950 F-24 Hr-AC	1.00	141	117	83.0	Possible light corrosion
Ti-6Al-2Cb-1Ta-0.8Mo	1950 F-1 Hr-AC	0.993	246	244	99.2	No corrosion
			Sheet Test Results			
Ti-4Al-3Mo-1V	1350 F-2 Hr-FC	0.114	145.4	139.1	95.6	No corrosion
Ti-8Mn	1300 F-1 Hr-FC	0.081	159.6	110.3	69.2	Definite corrosion

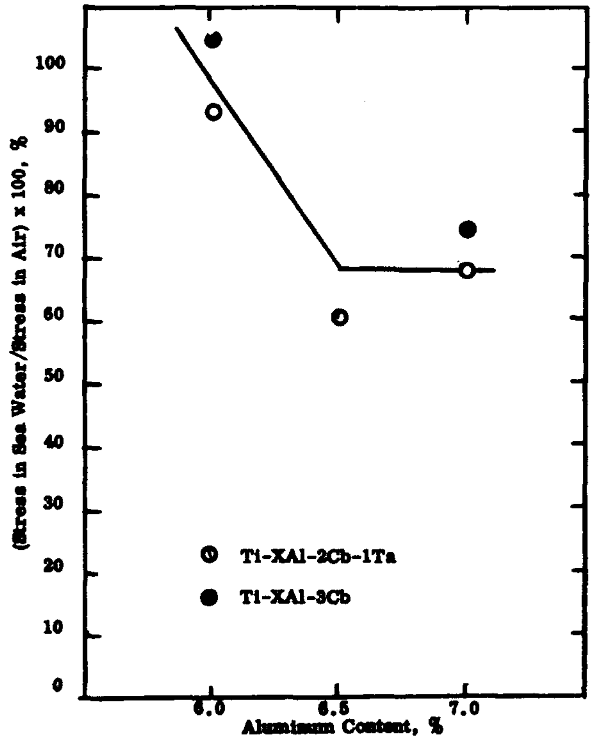

FIGURE 15. EFFECT OF ALUMINUM CONTENT ON THE SEAWATER TO AIR FAILURE STRESS RATIO OF BETA-ANNEALED PLATE(39)

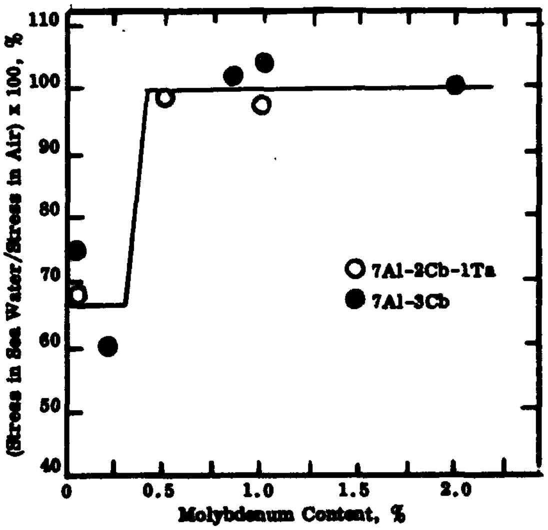

FIGURE 16. EFFECT OF MOLYBDENUM CONTENT ON THE SEAWATER TO AIR FAILURE STRESS RATIO OF BETA-ANNEALED PLATE(39)

TABLE 13. EFFECT OF SEAWATER ON COMPOSITIONAL VARIATIONS OF 7Al-2Cb-1Ta ALLOY[1](9,38)

Heat Treatment	6Al-2Cb-1Ta			6Al-3Cb			7Al-3Cb			7Al-3Cb-0.2Mo[2]			7Al-3Cb-0.8Mo[2]		
	Sn ksi	Time min	Sensitive?[3] (Fracture Appearance)	Sn ksi	Time min	Sensitive? (Fracture Appearance)	Sn ksi	Time min	Sensitive? (Fracture Appearance)	Sn ksi	Time min	Sensitive? (Fracture Appearance)	Sn ksi	Time min	Sensitive? (Fracture Appearance)
As-Received	131	9	Yes	228	-	(4)	86	<1	Yes	143	3	Yes	179	12	No
1950 F, 1-Hr AC	147	3	Yes	215	<1	No	111	3	Yes	135	12	Yes	212	6	No
1950 F, 1-Hr WQ	178	<1	Yes	(5)	6	No	197	3	No	220	3	No	252	2	No
1920 F, 1-Hr FC							97	2	Yes	80	3	Yes	(5)	-	Yes
1920 F, 1-Hr FC + 1100 F, 2-Hr AC							96	10	Yes	88	9	Yes	81	2	Yes
1920 F, 1-Hr AC + 1100 F, 2-Hr AC							105	6	Yes	80	12	Yes	83	15	Yes
1920 F, 1-Hr WQ + 1100 F, 2-Hr AC							97	3	Yes	99	6	Yes	142(5)	3	No

[1] Specimens 1/2 x 1/2 x 4 inches were notched to a depth of 10 percent at their mid-length with a saw cut and statically loaded in a sea-water environment. The specimens were initially stressed to 50,000 psi, and the stress was increased by increments of 6000 psi every 5 to 10 minutes until failure.

[2] Variation in the notch acuity of the 0.2- and 0.8-percent alloys, in the 1920 F, 1-hr AC heat treated condition gave the following results:

	Ti-7Al-3Cb-0.2Mo			Ti-7Al-3Cb-0.8Mo		
	Sn ksi	Time min	Sensitivity?	Sn ksi	Time min	Sensitivity?
Machined Notch (20% a/d)	(5)	24	Yes	184	25	No
Fatigue Crack (25-30% a/d)	143	3	No	176	3	No

[3] A material is considered "sensitive" when the fractured specimen contains a zone characteristic of sea-water embrittlement.

[4] Specimen did not fail.

[5] Specimen failed outside the notch.

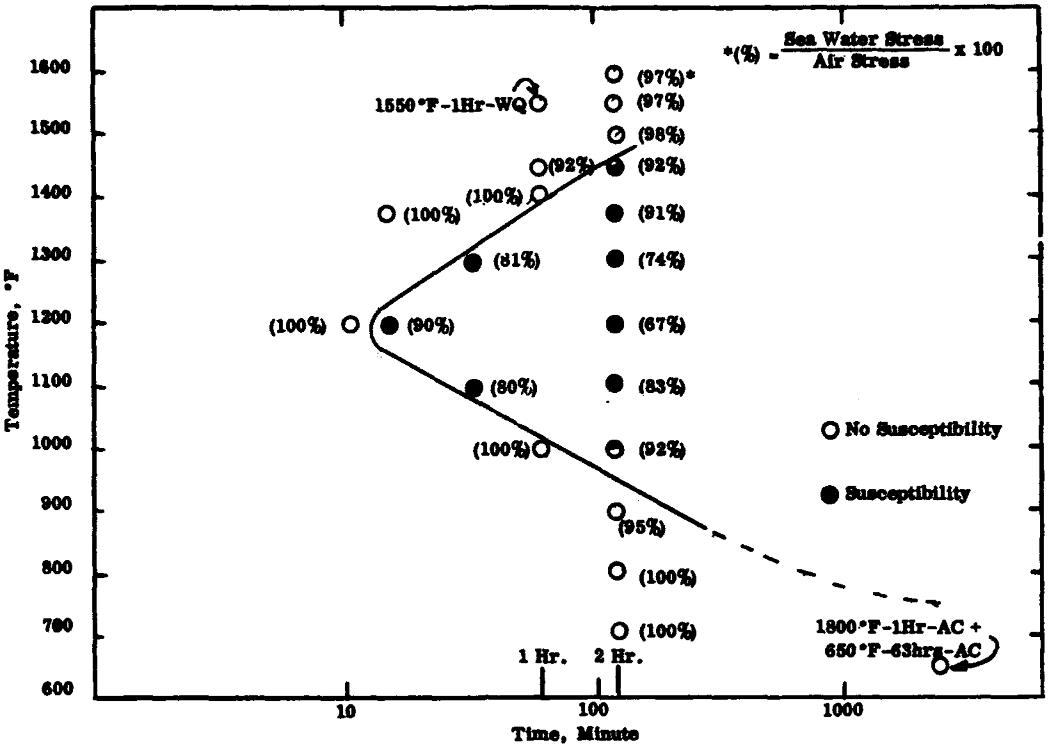

FIGURE 17. EFFECT OF EXPOSURE TEMPERATURE AND TIME ON THE STRESS-CORROSION CRACKING OF Ti-8Al-1Mo-1V PLATE IN ROOM TEMPERATURE SYNTHETIC SEAWATER(39)

TABLE 14. EFFECT OF ANNEALING TEMPERATURE AND QUENCHING ON SALT-WATER SUSCEPTIBILITY OF Ti-8Al-1Mo-1V(39)

	Failure Stress at Crack Root, ksi					
	Air Cool			Water Quench		
Treatment(a)	Air	Seawater	Ratio, %	Air	Seawater	Ratio, %
1450 F - 1 hr	267	235	88	259	250	96
1550 F - 1 hr	248	223	90	257	258	100
1675 F - 1 hr	267	247	92	256	254	99
1700 F - 1 hr	252	235	93			
1750 F - 1 hr	250	229	92			
1800 F - 1 hr	250	257	>100			
1850 F - 1 hr	258	258	100			
1950 F - 1 hr	219	214	98			

(a) When as received a failure stress of 246 ksi in air and 174 ksi in seawater for a ratio of 71 percent is reported.

TABLE 15. EFFECT OF ANNEALING TEMPERATURE AND COOLING RATE ON THE FRACTURE APPEARANCE OF Ti-6Al-4V PLATE TESTED IN SYNTHETIC SEAWATER(a)(39)

Heat Treatment Temperature and Time	Fracture Appearance(b) For Water Quench	For Air Cool
1300 F - 1 hr		Yes
1450 F - 1 hr		Yes
1550 F - 1 hr	V.S.	-
1600 F - 1 hr		Yes
1650 F - 1 hr		Yes
1700 F - 1 hr		V.S.
1750 F - 1 hr	No	No
1800 F - 1 hr		No
1850 F - 1 hr		No

(a) Ht. 21149, 0.75 in. thick; all specimens tested by step loading in three point bend.

(b) Yes indicates a change in fracture texture adjacent to fatigue crack,
No indicates no change in fracture texture adjacent to fatigue crack,
V.S. indicates very slight change in fracture texture adjacent to fatigue crack.

TABLE 16. EFFECT OF HEAT TREATMENT ON THE FRACTURE STRESS OF Ti-6Al-4V IN AIR AND SEAWATER(39)

Heat No.	Thick, in.	Heat Treatment	Nominal Fracture Stress at Crack Root In Air, ksi	In Sea Water, ksi	$\frac{S_{s.w.}}{S_{air}}$ x 100	Fracture(a) Surface Appearance
292030(b)	0.750	1450 F - 1 hr - FC	212	170	80%	Yes
292030(b)	0.750	1750 F - 2 hr - AC	287	335	>100%	No
21149(b)	0.750	1450 F - 1 hr - FC	183	143	78%	Yes
Ditto	Ditto	1750 F - 1 hr - AC + 1200 F - 1/2 hr - AC	248	228	92%	V.S.
"	"	1750 F - 1 hr - AC + 1300 F - 1/2 hr - AC	260	235	89%	Ditto
"	"	1750 F - 1 hr - AC + 1400 F - 1/2 hr - AC	266	250	91%	"
"	"	1750 F - 1 hr - AC + 1500 F - 1/2 hr - AC	245	241	100%	"
"	"	1750 F - 1 hr - AC + 1650 F - 1/2 hr - AC	273	263	97%	"

(a) V. S. - Very slight evidence of seawater attack.
Yes - Good evidence of seawater attack.
No - No evidence of seawater attack.

(b) Plate tested at loading rate in 4 point bend of about 6 ksi per minute.

The microstructure then became needlelike alpha (i.e., "martensite"). This material became sensitive if again heated at 1100 F, with no apparent change in microstructure.

The fracture of titanium specimens can be both intergranular and transgranular.(38)

Effect of Sheet Thickness

The degree of susceptibility of an alloy which is sensitive to salt-water cracking is affected by the specimen thickness. Most reproducible results are obtained for plate of 1/2- to 1-inch thickness. In thin sections, the specimen tends to rupture in full shear, masking the effects of corrosion. This can be shown by Figure 18.(35)

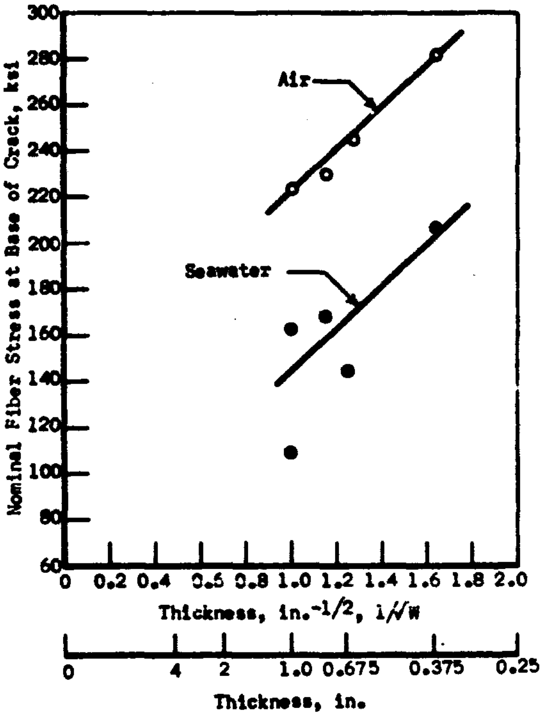

FIGURE 18. EFFECT OF PLATE THICKNESS AND TESTING MEDIA ON THE NOMINAL FIBER STRESS AT FAILURE IN PRE-CRACKED BETA-ANNEALED Ti-7Al-2Cb-1Ta ALLOY, THREE-POINT BEND SPECIMENS(35)

For duplex-annealed Ti-8Al-1Mo-1V, susceptibility is reported for sheet of 0.045- to 0.050-inch thick, but not for 0.025-inch sheet.(5,37) Mill-annealed Ti-6Al-4V is not susceptible in sheet thicknesses of 0.050 to 0.055 inch.(37,39) Susceptibility is reported for mill-annealed Ti-6Al-4V at a thickness of 0.500 inch(37) and susceptibility for this alloy may extend in thicknesses down to about 0.125 inch.

Considerable work is now under way to develop heat treatments which will produce maximum resistance to accelerated crack propagation for these and other alloys and to define the limits of gage thickness over which this susceptibility extends.

Effect of Strain Rate

Some titanium alloys appear to be sensitive to the rate of loading of precracked specimens. For example, Ti-6Al-4V shows less susceptibility to stress cracking in salt water when the specimen is loaded in steps than when it is loaded to a fixed value and subjected to a constant load.(39,41)

This is somewhat related to the internal relaxation and redistribution of stress at stress raisers in a material. Some metals readily distribute these stresses and therefore show no effect of rate of strain. Other metals do not redistribute the stresses at all, and thus behave in a brittle manner with low fracture-toughness.

Rapid loading of precracked Ti-6Al-4V samples caused failure at a stress-intensity of 31 ksi √in. in salt water. By step-loading an identical specimen (1 ksi √in. each 8 minutes), failure did not occur in salt water until a stress intensity of 51 ksi √in. was reached. A similar result was also shown in highly oxidizing nitrogen tetroxide liquid. When step-loaded at 2.5 ksi √in. or less every 4 to 8 minutes, failure occurred at about 80 ksi √in. However, loading from 62.5 to 69 ksi √in. in about 1 minute resulted in almost immediate failure.(42)

In long-term step-loading tests in air and seawater, the failure stress was found to increase by 15 percent when samples were step-loaded each hour, and by 30 percent when samples were step-loaded each 60 to 120 hours.(39) See Table 17. In order to minimize the effect of strain rate, a constant load procedure was evaluated. A loading rate of about 6 ksi/minute was used above about 50 percent of the estimated fracture stress.

TABLE 17. EFFECT OF TESTING PROCEDURE ON THE FAILURE STRESS OF Ti-6Al-4V SHEET(a)(39)

	Failure Stress at Crack Root, ksi	
Test Procedure	In Air	In Seawater
Direct load to failure	158	187
Step load every hour(b)		232
Step load every 60 to 120 hours(b)	243	265

(a) Heat 30695; 0.125 in. thick.

(b) Step loaded approximately 20 ksi starting at about 90 ksi.

A similar sensitivity to strain rate has been reported for Ti-4Al-3Mo-1V.(41) This suggests that other alpha-beta titanium alloys might also behave in this manner.

Effect of Grain Direction

Table 18 shows that the transverse grain direction in both the Ti-8Al-1Mo-1V and Ti-6Al-4V alloy has lower fracture toughness in both air and salt water. This would be expected, based on other mechanical properties of materials. It is interesting to note that the fracture orientation of some titanium alloys was also different for air and salt-water exposure.(38,41,42)

TABLE 18. STRESS INTENSITY AT FAILURE FOR LONGITUDINAL AND TRANSVERSE TITANIUM IN AIR AND SALT WATER(41)

		Stress Intensity at Failure, ksi $\sqrt{\text{in.}}$(a)			
		Air		3-1/2 % Salt Water	
Alloy	Condition	Longitudinal	Transverse	Longitudinal	Transverse
Ti-8Al-1Mo-1V	Mill Anneal	50	24	28	17
Ti-8Al-1Mo-1V	Duplex Anneal	62	53	36	20
Ti-6Al-4V	Mill Anneal	72	63	35-70	31-37

(a) Step-loaded.

Welding

A few preliminary experiments have been reported on the effect of weldments on the fracture toughness of susceptible alloys in seawater.(38) In one case, Ti-7Al-2Cb-1Ta plate was beta-annealed and water quenched to obtain maximum resistance to stress-corrosion cracking. This plate was then welded, and subjected to salt-water fracture tests. However, failure initiated at the toe of the weld and propagated into the base plate at a stress level comparable to normally susceptible material. Stress relieving a similar weldment at 1200 F for 2 hrs AC gave no improvement.

Similar tests on Ti-6Al-4V (alpha-beta rolled) and Ti-7Al-2.5Mo (alpha-beta rolled + 1735 F/1 hr/WQ + 1100 F/2 hr/AC), followed by welding, gave no failures up to 128 and 175 ksi nominal fiber stress, respectively.

Effect of pH and Temperature of Salt Solutions

Varying the pH of a 3-1/2 percent NaCl solution between 4.5 and 8 has little effect on the susceptibility of Ti-8Al-1Mo-1V and Ti-6Al-4V alloys. At a pH above or below these values the alloys appear to have an increased susceptibility as shown in Table 19.(37,41) These alloys are slightly more susceptible to cracking at 32 F than at room temperature or above. See Table 19.

Fatigue

In preliminary low-cycle (1 cpm) corrosion fatigue studies in seawater, the results were found to parallel static tests for Ti-7Al-2Cb-1Ta, Ti-7Al-2.5Mo, and Ti-6Al-2Sn-1Mo-1V alloys.(38) Smooth, notched, and fatigue-cracked specimens were used. Only the Ti-7Al-2Cb-1Ta alloy showed susceptibility to corrosion fatigue. Susceptibility was observed for all three specimen configurations. The fracture was typical of a stress-corrosion crack rather than a fatigue-type crack.

Other Liquids

The effects of several liquids on the stress-corrosion cracking of several precracked titanium alloys are shown in Table 20. The addition of small amounts of $FeCl_3$, $AlCl_3$, or Duponol wetting agent to salt water does not significantly alter the behavior of Ti-8Al-1Mo-1V or Ti-6Al-4V in salt water.

Little susceptibility is noted for several acids. In fact, as one would expect, stress intensity values somewhat higher than in air are sometimes found with highly oxidizing environments such as nitric acid.

In short-term tests, nitrogen tetroxide gives about the same stress intensity values as in air.(42) However, after a 12-day exposure to N_2O_4, Ti-6Al-4V failed in a brittle manner typical of stress-corrosion cracking. As noted earlier in this note, the Ti-6Al-4V alloy does appear susceptible to stress corrosion by liquid N_2O_4 and efforts are under way to define the conditions under which this behavior can occur.

The limited data of Table 20 indicate that the susceptibility of titanium alloys to crack propagation may be greater in tap and distilled water than it is in air.

Some susceptibility to cracking is indicated by certain hydrocarbons. Methyl and dodecyl alcohol appear to increase the crack propagation susceptibility of some titanium alloys, whereas kerosene and acetone do not. It is suggested that this variation may be due to the conductivity of the hydro-carbons, e.g., water content, since electrochemical reactions may be controlling.(41)

Of the liquid metals, mercury severely lowers the stress intensity factor for titanium alloys. Mercury apparently causes as great or greater a susceptibility than does salt water.(41) Gallium shows no adverse effect.

Postulated Mechanisms

Stress-corrosion cracking is normally considered to be a two-step process involving (1) initiation phase and (2) propagation of the crack. The use of a precracked specimen essentially eliminates the initiation stage. The mechanism of the cracking, however, appears to be consistent with the several theories advanced to explain the mechanism of stress-corrosion cracking in metals. They are:

1. Electrochemical. The electrochemical theory proposes that the initiation and propagation of the crack are purely electrochemical dissolution of continuous highly localized paths which are anodic to the bulk of the material. These paths may be preexisting, such as along grain boundaries, or they may form as a result of phase changes resulting either from high stresses at the apex of the crack on the diffusion of corrosion-produced hydrogen into the metal. High stresses such

TABLE 19. EFFECT OF pH AND TEMPERATURE ON STRESS INTENSITY AT FAILURE OF Ti-8Al-1Mo-1V AND Ti-6Al-4V IN 3-1/2% NaCl WATER

Alloy	pH	Temperature, F	Approximate Stress Intensity, ksi $\sqrt{\text{in.}}$	Reference No.
Ti-8Al-1Mo-1V	-	RT(a)	50(b)	41
	4.5	RT	28	41
	7	RT	29	41
	9	RT	26	41
	11	RT	25	41
	7	32	27	41
	7	RT	29	41
	7	150	29	41
Ti-6Al-4V	-	RT	62-72(b)	37,41
	2	RT	46	41
	4	RT	50	41
	4.5	RT	53	37
	6	RT	54	41
	7	RT	54	37
	8	RT	54	41
	9	RT	48	37
	10	RT	31	41
	11	RT	45	37
	7	32	49	37
	7	RT	54	37

(a) Room temperature.

(b) Air.

TABLE 20. EFFECT OF LIQUID ENVIRONMENT ON CRACK PROPAGATION OF TITANIUM ALLOYS

Alloy	Condition	Grain Direction	Environment	Stress Intensity ksi $\sqrt{\text{in.}}$(a)		Reference No.
Ti-8Al-1Mo-1V	Mill Anneal	L	3-1/2% NaCl + 0.5% $FeCl_3$, pH 2.2	30	(47)	41
	Ditto	L	3-1/2% NaCl + 1.0% $AlCl_3$, pH 7.0	26	(47)	41
	"	L	3-1/2% NaCl + 0.1% Duponol	30	(47)	41
	"	L	3-1/2T $CaCl_2$, pH 8.2	25	(47)	41
	"	L	2% HNO_3, pH 0.8	55	(47)	41
	"	L	0.95% H_2SO_4, pH 1	43-50	(47)	41
	"	L	N_2O_4, 125 F + Helium to 250 psig	65	(47)	42
	"	L	Moist Air	39	(47)	42
	"	L	H_2, 1750 psi	49	(47)	42
	"	L	Kerosene	50	(47)	41
	"	L	Acetone	52	(47)	41
	"	L	Trichloroethylene, trace sealer	34	(47)	41
	"	L	Dodecyl Alcohol	43	(47)	41
	"	T	Dodecyl Alcohol	21	(29)	41
	"	L	Methyl Alcohol	31	(47)	41
	"	L	Mercury	26	(47)	41
	"	L	Gallium, 90 F	49	(47)	41
	"	L	Deionized Water	35	(47)	41
	"	T	Deionized Water	19	(29)	41
	Duplex Anneal	T	Water	32	(55)	37
	Ditto	T	50% HNO_3	32	(55)	37
	"	T	2% HF	30	(55)	37
	1450 F/1 hr/AC or WQ 1100 F/8 hr/AC	L	Kerosene	41	(41)	37
	1850 F/1 hr/WQ + 1100 F/8 hr/AC	L	Kerosene	31	(<37)	37
	1/8 in. sheet	-	Distilled Water	25	(<50)	36

TABLE 20. (Continued)

Alloy	Condition	Grain Direction	Environment	Stress Intensity ksi $\sqrt{in.}$(a)		Reference No.
Ti-6Al-4V	Mill Anneal	L	3-1/2% NaCl + 0.5% $FeCl_3$, pH 2.2	49	(72)	41
	Ditto	L	3-1/2% NaCl + 1.0% $AlCl_3$, pH 7.0	46	(72)	41
	"	L	3-1/2 % NaCl + 0.1% Duponol	46	(72)	41
	"	L	N_2O_4, 125 F + Helium to 250 psig	79	(70)	42
	"	L	N_2O_4, 183 F + Helium to 250 psig	78	(70)	42
	"	L	N_2O_4, 125 F + 0.5% Water, He to 250 psig	88	(70)	42
	"	L	N_2O_4, 125 F + 0.25% HCl, He to 250 psig	83	(70)	42
	"	L	N_2O_4, 125 F, He to 80 psig	70(b)	(70)	42
	"	L	Kerosene	71	(72)	41
	"	L	Dodecyl Alcohol	67	(72)	41
	"	L	Methyl Alcohol	70	(72)	41
	"	L	Mercury	22	(72)	41
	"	T	Tap Water	41	(51)	37
Ti-7Al-2Cb-1Ta	As Received	-	Tap Water	103(c)	(183)(c)	38
	Ditto	-	Distilled Water	91(c)	(183)(c)	38
	"	-	NaOH solution, pH 10	125(c)	(183)(c)	38
	"	-	Distilled Water	63	(<100)	36
	"	-	Tap Water	57	(<100)	36

(a) Air value in parentheses.

(b) Failure after 12 days.

(c) Nominal fiber stress, ksi.

as those existing at the tip of a crack also can shift the potential in the less noble direction.

2. <u>Mechanical, Mechanical-Electrochemical</u>. It Has been proposed that the only role of corrosion is to initiate a pit or other stress raiser, which intensifies the stress to a point where the tensile strength of the material is exceeded and thus mechanical fracture of the metal occurs. Proponents of this theory also point out that oxides and other corrosion products formed within the pit or crack can, and in fact do, result in a wedge action which results in mechanical rupture of the metal at the tip of a crack.

3. <u>Stress-sorption</u>. This theory proposes that surface active ions which absorb in mono- or double layer act to set up charges on the metal surface. These charges reduce the binding energy of the atoms which are then ruptured by the high stress.

The available evidence strongly suggests that the mechanism is electrochemical in nature. For example, studies have shown that cathodic protection can prevent crack propagation and can arrest propagation when applied to a moving crack.(41) The electrochemical behavior of crack propagation is shown in Figure 19. The effect of applied potential on the susceptibility of Ti-8Al-1Mo-1V and Ti-6Al-4V to salt-water cracking can be seen. Note that the application of anodic (+) potential (anodic dissolution) does not seem to increase the susceptibility to cracking.(41)

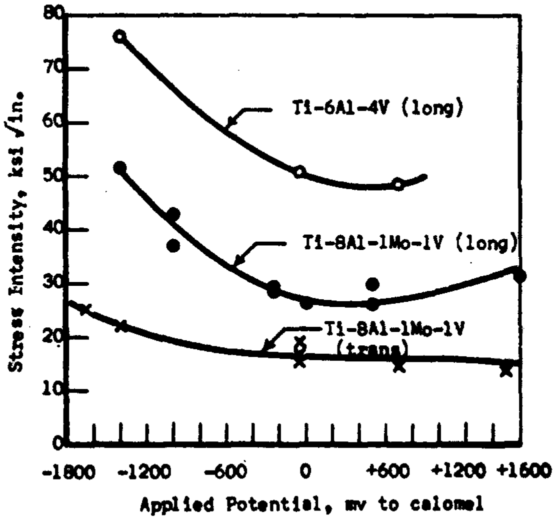

FIGURE 19. THE EFFECT OF APPLIED POTENTIAL ON THE STRESS INTENSITY FACTOR TO CAUSE FAILURE IN 3-1/2 PERCENT SALT WATER(41)

Applied Potential, mv to calomel

Hydrogen embrittlement does not appear to be involved in the mechanism since the generation of hydrogen by cathodic protection and cathodic charging for 5 hours at -1400 mv did not result in a brittle fracture. In addition, no differences in susceptibility were observed for Ti-8Al-1Mo-1V containing 20 to 150 ppm H_2.

The nature of the anodic (corroding) phase of the crack was not determined, but it was suggested that the phase may be produced during the test rather than preexisting. Potential measurements during step-loading of some highly susceptible Ti-8Al-1Mo-1V specimens show potential peaks just after each load is applied, and prior to failure. This potential rise may be caused by:

1. Exposure of fresh metal by rupture of the oxide film
2. Microcracking
3. Localized stress concentration
4. Localized phase changes under stress (hydride precipitation, Ti_3Al formation, etc).

The relationship between heat treatment of high aluminum-titanium alloys, precipitation of Ti_3Al, and cracking susceptibility, as discussed previously, adds evidence to the belief that Ti_3Al precipitation may be related to the path of the crack.

Although the mechanical, mechanical-electrochemical and stress-sorption theories can not be ruled out on the basis of the present information, they appear less likely than the electrochemical theory.

REFERENCES

(1) Stough, D. W., Fink, F. W., and Peoples, R. S., "The Stress Corrosion and Pyrophoric Behavior of Titanium and Titanium Alloys", TML Report No. 84, Defense Metals Information Center, Battelle Memorial Institute, Columbus, O., (September 15, 1957).

(2) Boyd, W. K., and Fink, F. W., "The Phenomenon of Hot-Salt Stress-Corrosion Cracking of Titanium Alloys", Report No. CR-117, National Aeronautics and Space Administration, Washington, D. C., under NASA Contract NASr-100(04) (October, 1964).

(3) Brown, B. F., "A New Stress-Corrosion Cracking Test Procedure for High-Strength Alloys", paper presented at the Sixty-Eighth Annual Meeting of the American Society for Testing and Materials, held in Lafayette, Indiana, June 13-18, 1965.

(4) Donachie, M. J., Jr., Danesi, W. P., and Pinkowrsh, A. A., "Effects of Salt Atmosphere on Crack Sensitivity of Commercial Titanium Alloys at 600-900 F", paper presented at the Fifth Pacific Area National Meeting of the American Society for Testing and Materials, Seattle, Washington, October 31 - November 15, 1965.

(5) Hatch, A. J., Rosenberg, H. W., and Erbin, E. F., "Effects of Environment on Cracking in Titanium Alloys", Titanium Metals Corp. of America, Henderson, Nevada, paper presented at 5th Pacific Area National Meeting of ASTM, Seattle, Washington, October 31 - November 5, 1965.

(6) Petersen, V. C., and Bomberger, H. B., "The Mechanism of Salt Attack on Titanium Alloys", Crucible Steel Company of America, paper presented at Fifth Pacific Area National Meeting of the ASTM, Seattle, Washington, October 31 - November 5, 1965.

(7) Wood, R. A., "The Ti-8Al-1Mo-1V Alloy", DMIC Report No. S-10, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio (April 1, 1965).

(8) Piper, D. E., and Fager, D. N., "The Relative Stress-Corrosion Susceptibility of Titanium Alloys in the Presence of Hot Salt", paper presented at the Fifth Pacific Area National Meeting of the ASTM, held in Seattle, Washington, October 31 - November 5, 1965.

(9) Heimerl, G. J., Braski, D. N., Royster, D. M., and Dexter, H. B., "Salt Stress Corrosion of Ti-8Al-1Mo-1V Alloy Sheet at Elevated Temperatures", NASA Langley Research Center, paper presented at the Fifth Pacific Area National Meeting of the ASTM, Seattle, Washington, October 31 - November 5, 1965.

(10) Avery, C. H., and Turley, R. V., "Chloride Stress Corrosion Susceptibility of High Strength Stainless Steel, Titanium Alloy, and Superalloy Sheet", Douglas Aircraft Co., Long Beach, California, ML-TDR-64-44, Vol I, (March, 1964) and Report No. ML-TDR-64-44, Vol II, "Stress Corrosion Data Summary", (May, 1964) under Air Force Contract AF 33(657)-8543.

(11) Martin, George, "Investigation of Long-Term Exposure Effects Under Stress on Supersonic Transport Structural Alloys", paper presented at the ASTM-ASME Panel on Structural Materials, Seattle, Washington, October 31 - November 5, 1965.

(12) Turley, R. V., and Avery, C. H., "Elevated-Temperature Static and Dynamic Sea-Salt Stress Cracking of Titanium Alloys", paper presented at the Fifth Pacific Area National Meeting of the ASTM, Seattle, Washington, October 31 - November 5, 1965.

(13) Larson, F. R., Miller, J., "A Time-Temperature Relationship for Rupture and Creep Stresses", Trans ASME, 52, p 765 (July, 1952).

(14) Braski, D. N., and Heimerl, G. J., "The Relative Susceptibility of Four Commercial Titanium Alloys to Salt Stress Corrosion at 550 F", NASA Technical Note, Report No. TND-2011, Langley Research Center, Langley Station, Hampton, Virginia (December, 1963).

(15) Logan, H. L., McBee, M. J., Bechtoldt, C. J., Sanderson, B. T., and Ugiansky, G. M., "The Mechanism of Stress Corrosion of Titanium Alloys Exposed Sodium Chloride at Elevated Temperatures", NBS Report 8690, U. S. Department of Commerce, National Bureau of Standards, Washington, D. C. (May 4, 1964).

(16) Rideout, S. P., Louthan, M. R., and Selby, C. L., "Basic Mechanisms of Stress-Corrosion Cracking of Titantium", paper presented at the Fifth Pacific Area National Meeting of the ASTM, held in Seattle, Washington, October 31 - November 5, 1965.

(17) Simenz, R. F., VanOrden, J. M., and Wald, G. G., "Environmental Effects Studies on Selected Titanium Alloys", Lockheed-Georgia Company, Burbank, California, paper presented at the Fifth Pacific Area National Meeting of the ASTM, held in Seattle, Washington, October 31 - November 5, 1965.

(18) Braski, D. N., "Preliminary Investigation of Effect of Environmental Factors on Salt Stress Corrosion Cracking of Ti-8Al-1Mo-1V at Elevated Temperatures", NASA Technical Memorandum, TMX-1048, Langley Research Center, Langley Station, Hampton, Virginia (December, 1964).

(19) Logan, H. L., McBee, M. J., Bechtoldt, C. J., Sanderson, B. T., and Ugiansky, G. M., "Chemical and Physical Mechanisms of Salt Stress-Corrosion Cracking of the Titanium 8-1-1 Alloy", paper presented at the Fifth Pacific Area National Meeting of the ASTM, held in Seattle, Washington, October 31 - November 5, 1965.

(20) Kirchner, R. L., and Ripling, E. J., "Diffusion of Corrosion Products in Hot Salt Stress-Corrosion Cracking of Titanium", Materials Research Laboratory, Inc., Richton Park, Illinois (October, 1965).

(21) Martin, George, "Stress Corrosion of Some Aircraft Materials at High Temperature", Materials Protection, 4 (8), pp. 23-26 (August, 1965).

(22) Pride, R. A., and Woodard, J. M., "Salt-Stress-Corrosion Cracking of Residually Stressed Ti-8Al-1Mo-1V Brake Formed Sheet at 550 F (561 K)", TMX-1082, NASA, Langley Research Center, Langley Station, Hampton, Virginia (April, 1965).

(23) Covington, L. C., and Early, F. R., "Methods of Protecting Titanium Against Hot Salt Stress Corrosion", Progress Report No. 21, Titanium Metals Corporation of America, West Caldwell, New Jersey, Special Summary Report Project 47-42 (August, 1964).

(24) Duttweiler, R. E., Wagner, R. R., and Antony, K. C., "An Investigation of Stress Corrosion Failures in Titanium Compressor Components", paper presented at the Fifth Pacific Area National Meeting of the American Society for Testing and Materials, Seattle, Washington, October 31 - November 15, 1965.

(25) Shlain, David, "Corrosion Properties of Titanium and Its Alloys", Bulletin 619, Bureau of Mines, U. S. Department of the Interior (1964).

(26) Boyd, W. K., Berry, W. E., and White, E. L., "Compatibility of Materials With Rocket Propellants and Oxidizers", DMIC Memo No. 201, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio (January 29, 1965).

(27) Mori, Kenji, Takamura, Akira, and Shimose Takaaki, "Stress Corrosion Cracking of Ti & Zr in HCl-Methanol Solutions", Corrosion, 22, pp. 29-31 (February, 1966).

(28) Tomashov, N. D., Al'tovskiy, R. M., and Vladimirov, V. B., "Study of the Corrosion of Titanium and Its Alloys in Methyl Alcohol Solutions of Bromine", Translation FTD-TT-63-672/1+2, pp. 221-233a, Translation Division, Foreign Technology Division WPAFB, Ohio, from Korroziya i Zashchita Konstruktsionnykh Metallichoskikh Materialov, Moscow (1961) DMIC No. 57587.

(29) "Nuclear Fuels and Materials Development", USAEC Report TID-11295, 2nd Ed. (September, 1962).

(30) Hallowell, J. B., Dunleavy, J. G., and Boyd, W. K., "Liquid-Metal Embrittlement", DMIC Technical Note, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio (April 9, 1965).

(31) Campbell, J. E., "Current Methods of Fracture-Toughness Testing of High-Strength Alloys With Emphasis on Plane Strain", DMIC Report No. 207, Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio (August 31, 1964).

(32) Stiegerwald, E. A., "Delayed Failures of High-Strength Steel in Liquid Environments", ASTM, 60 (1960).

(33) Brown, B. F., Lennox, T. J., Jr., Newbegin, R. L., Peterson, M. H., Smith, J. A., and Waldron, L. J., "Marine Corrosion Studies", NRL Memorandum Report 1574, Second Interim Report of Progress, U. S. Naval Research Lab., Washington, D. C. (November, 1964).

(34) Private communication from Titanium Metals Corporation of America.

(35) Private communication from Reactive Metals Incorporated to J. D. Jackson (August 25, 1965).

(36) Brown, B. F., Lennox, T. J., Jr., Newbegin, R. L., Peterson, M. H., Smith, J. A., and Waldron, L. J., "Marine Corrosion Studies", NRL Memorandum Report 1634, Third Interim Report of Progress, U. S. Naval Research Lab., Washington, D. C. (July, 1965).

(37) Private communication from Boeing Airplane Company to Dr. R. I. Jaffee (July 30, 1965).

(38) Lane, I. R., Jr., Cavallero, J. L., and Morton, A. G. S., "Fracture Behavior of Titanium in the Marine Environment ", MEL R&D Phase Report 231/65, U. S. Navy Marine Engineering Laboratory, Annapolis, Maryland (July, 1965); see also Lane, I. R., Jr., Cavallero, J. L., and Morton, A. G. S., "Sea-Water Embrittlement of Titanium", paper presented at the Fifth Pacific Area National Meeting of the American Society for Testing and Materials, Seattle, Washington, October 31 - November 5, 1965.

(39) "A Study of the Stress Corrosion Cracking of Titanium Alloys in Sea Water With Emphasis on the Ti-6Al-4V and Ti-8Al-1Mo-1V Alloys", Research Report No. R471, Project No. 93002, Reactive Metals, Inc., Niles, Ohio (October 18, 1965).

(40) Crossley, F. A., and Carew, W. F., "Embrittlement of Ti-Al Alloys in the 6 to 10 Pct Al Range", J. of Metals, 209, pp. 43-46 (January, 1957).

(41) Williams, D. N., Wood, R. A., White, E. L., Boyd, W. K., and Ogden, H. R., "Studies of the Mechanism of Crack Propagation in Salt Water Environments of Candidate Supersonic Transport Titanium Alloy Materials", Final Report SST-66-1, Battelle Memorial Institute, Columbus, Ohio, under Federal Aviation Agency Contract FA-SS-66-1 (January, 1966).

(42) Unpublished DMIC data, J. D. Jackson (December, 1965).