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CORROSION OF TITANIUM

DEFENSE METALS INFORMATION CENTER
BATTELLE MEMORIAL INSTITUTE
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CORROSION OF TITANIUM

J. D. Jackson and W. K. Boyd*

SUMMARY

This memorandum summarizes information that has become available to the Defense Metals Information Center since 1960 on the general corrosion behavior of titanium and titanium alloys. It supplements similar information contained in Bureau of Mines Bulletin 619, which covered the period through 1960. Collectively, these two publications provide an up-to-date review on the performance of titanium and its alloys in various salt solutions, mineral acids, organic compounds, gases, and liquid metals.

Since 1960, a number of field tests have been performed on titanium in various corrosive environments. This memorandum points out those service applications where the use of these materials is likely to be limited, as well as many applications where their use has been quite successful.

This memorandum also identifies certain media and conditions under which stress-corrosion cracking behavior has been observed in titanium and/or titanium alloys. These media include certain solutions of NaCl, H_2SO_4, HCl, dry red fuming nitric acid, methanol containing H_2SO_4 or HCl, certain grades of N_2O_4, molten cadmium, mercury, silver, and silver-containing compounds and alloys. Experiences with the stress-corrosion cracking of titanium and its alloys in hot salt and on the accelerated crack propagation of these materials in selected environments are not included in this memorandum, these having recently been summarized in another DMIC publication.

INTRODUCTION

The use of titanium has grown remarkably since since it first achieved commercial status in the early 1950's. By the end of 1965, the total annual mill production of titanium had reached nearly 19 million pounds, of which about 90 percent went to aircraft and aerospace applications. This usage has resulted largely from the high strength-to-weight ratio and good corrosion resistance of titanium and its alloys.

To keep pace with the vast amount of corrosion information that has been generated since the early 1950's, the Defense Metals Information Center generated a series of 17 reports, memoranda, and technical notes that dealt wholly or in part with the performance of titanium and its alloys. These are listed below:

DMIC No.	Date	Title
		REPORTS
57**	Oct. 29, 1956	The Corrosion of Titanium (PB 121601, $4.75)
84**	Sept. 15, 1957	The Stress Corrosion and Pyrophoric Behavior of Titanium and Titanium Alloys (PB 121635)
216	May 10, 1965	Corrosion of Materials by Ethylene Glycol-Water (AD 466284)
224	Jan. 3, 1966	Ignition of Metals in Oxygen
		MEMORANDA
89	Mar. 6, 1961	Summary of Present Information on Impact Sensitivity of Titanium When Exposed to Various Oxidizers (PB 161239, $0.50)
151**	Apr. 27, 1962	Compatibility of Propellants 113 and 114 B2 With Aerospace Structural Materials (AD 275427, $0.50)
163	Jan. 15, 1963	Reactivity of Metals With Liquid and Gaseous Oxygen (AD 297124, $0.75)
173	Aug. 1, 1963	Reactivity of Titanium With Gaseous N_2O_4 Under Conditions of Tensile Rupture (AD 419555, $0.50)
201	Jan. 29, 1965	Compatibility of Materials With Rocket Propellants and Oxidizers
209	Oct. 5, 1965	Materials for Space-Power Liquid Metals Service
		TECHNICAL NOTES
	July 29, 1964	Permeability of Titanium to Hydrogen
	April 9, 1965	Liquid Metal Embrittlement
	July 9, 1965	The Effects of Silver on the Properties of Titanium
	Feb. 1, 1966	The Stress-Corrosion and Accelerated Crack-Propagation of Titanium and Titanium Alloys
	Feb. 4, 1966	Reaction of Titanium With Gaseous Hydrogen at Ambient Temperatures
	Apr. 11, 1966	Stress-Corrosion of Ti-6Al-4V in Liquid Nitrogen Textroxide

As indicated by their titles, most of these publications were concerned with behavior of titanium in specific media or environments. In 1964, the first and only DMIC report[1]* that dealt with the general corrosion behavior of titanium and its alloys (Report No. 57) was superseded by U. S. Bureau of Mines Bulletin 619, "Corrosion of Titanium and Its Alloys", by David Schlain.[2] This bulletin provides an excellent and comprehensive summary of general corrosion data, most of which were obtained prior to 1960. This present DMIC memorandum represents an effort to summarize similar corrosion data that have been generated since that time. Thus, taken together, Bureau of Mines Bulletin 619 and this memorandum provide what is believed to be a reasonably complete and up-to-date summary of the general corrosion behavior of titanium and its alloys in various salt solutions, mineral acids, organic compounds, gases, and liquid metals.

So far as other DMIC publications are concerned, the data in this memorandum supplement

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**DMIC supply exhausted; copies may be ordered from CFSTI.

* References are listed on pages 38 to 41.

but do not supersede or include the detailed data contained in the above-listed technical notes. The only exception is that no attempt has been made in the present memorandum to summarize or review those data that appeared in the technical note of February 1, 1966, relating to the hot-salt stress-corrosion cracking or crack propagation behavior of titanium and titanium alloys. Much new information on these two subjects is currently being developed on programs associated with the development of the supersonic transport by the FAA and the deep-diving submersible vehicle by the Navy. Consequently, it is the intent of DMIC to undertake a complete and separate review of the hot-salt and crack propagation data toward the end of 1966 by which time a reasonably complete summary of this new information can be made.

CORROSION IN SALT SOLUTIONS

General Corrosion

In general, titanium and its alloys show excellent corrosion resistance to seawater, salt water, and other salt solutions over a wide range of temperature and concentration. Much of the data supporting these conclusions were obtained prior to 1960, and have been summarized in detail by Schlain.(2)

For reference purposes, the corrosion rate of unalloyed titanium in seawater at ambient temperature is low, about 0.02 mils per year.(3) Several titanium alloys, Ti-75A, Ti-6Al-4V, Ti-5Al-2.5Sn, and Ti-3Al-11Cr-13V, were completely resistant to deep ocean exposure for times to 197 days in stressed or unstressed condition.(4) The exposure was made at 2340-foot depth in the Pacific Ocean off California. Some specimens were partly submerged in the mud at the bottom. The salinity was 34.37 g NaCl/kg of seawater, pH 7.46, with an oxygen content of 0.60 ppm. The temperature averaged 45 F with a velocity of about 0.3 knot. Stress specimens were stressed from 35 to 75 percent of yield strength with no indication of failure after 197 days.

Table 1 gives corrosion rates for various wrought and powder-metallurgy produced titanium materials in calcium chloride solutions. Note that "regular" (i.e., presumably, conventionally melted and rolled material) unalloyed titanium shows about the same resistance as the other materials. Table 2 gives corrosion rates of several titanium-molybdenum-palladium-carbon alloys in several $CaCl_2$ solutions as well as in various mineral acid solutions. Note that, in 350 F, 73 percent $CaCl_2$, severe pitting occurs in unalloyed titanium but not in alloys containing palladium or molybdenum.

The corrosion resistance of several welded titanium alloys was investigated in chloride salt solutions.(5) The corrosion rates are shown in Table 3. Exposure times of 705 to 932 hours were used.

The corrosion resistance of the welded specimens was found to be comparable to the base metal. Welded titanium alloy OT4-2 (5.5-6.7Al, 1.0-2.3Mn) was equally resistant to the media shown. Titanium was severely corroded in 75 percent $CaCl_2$ at 352 F, however.

Other studies were made using $MgCl_2$-$6H_2O$ at 374 to 379 F.(5) This salt decomposes to Mg_2OCl_2 and HCl. In 400 to 500-hour tests, unalloyed titanium weldments suffered corrosion of 70 to 200 mpy. Weldments of Ti-3Al-1.5Mn were more resistant, about 12 mpy, and welded OT4-2 corroded at 2.4 mpy.

Table 4 presents additional data for unalloyed titanium in various chloride solutions.

Table 5 shows the effect of pH on the corrosion resistance of unalloyed titanium to boiling 23 percent NaCl.(8) The solution was probably acidified with HCl, showing the effects of increasing HCl content.

Crevice and Pitting Attack

Titanium has been shown to be subject to crevice attack in high-temperature salt solutions.(3,6,9,10) With NaCl the severity and frequency of the attack increase with increase of salt concentration above a temperature of 212 F. The frequency of attack increases with exposure time. The attack increases with increased acidity but has been observed at a pH as high as 8.7.

Several alloys also show some susceptibility to crevice attack.(9) These included:

Ti-3.5Al-4.9Cr-0.2Fe
Ti-4.2Al-4.6Mn-0.3Fe
Ti-6.4Al-4.2V-0.2Fe
Ti-7.4Al-2.0Cb-1.1Ta-0.2Fe
Ti-8.2Al-8.5Zr-0.7Cb-0.5Ta.

TABLE 1. EXPOSURE IN CALCIUM CHLORIDE SOLUTIONS(3)

	Corrosion Rates, mils per year, For Indicated Exposure*										
	1	2	3	4	5	6	7	8	9	10	11
Ti(a)	0.0003	0.02	0.1	16(j)	0.04	0.03	84(j)	83(j)	–	10(j)	10(k)
Ti(b)	Nil	–	–	–	–	–	–	–	–	–	–
Ti(c)	0.03	–	–	–	–	–	–	–	–	–	–
Ti(d)	0.06	–	–	–	–	–	–	–	–	–	–
Ti(e)	–	–	–	19(i)	–	–	>300(m)	–	–	–	–
Ti(f)	–	–	–	0.5	–	–	53(j)	–	–	–	–
Ti(g)	–	–	–	–	–	–	30(j)	–	–	–	–
Ti(h)	–	–	–	–	–	–	43(j)	–	–	–	–
Ti(i)	–	–	–	–	–	–	–	78(m)	–	–	–

(a) Regular titanium.
(b) Powder metallurgy titanium – 95 to 99 percent density.
(c) Powder metallurgy titanium – 95 to 99 percent density.
(d) Powder metallurgy titanium – 95 to 99 percent density.
(e) Titanium chemically impregnated with H_2 to approximately 427 ppm. Skin concentration of H_2 estimated to be 50,000 ppm.
(f) Titanium vacuum annealed to 42 ppm H_2.
(g) Titanium vacuum annealed to 44 ppm H_2.
(h) Titanium vacuum annealed to 44 ppm H_2 and then platinum plated to a thickness of 3 microinches.
(i) Platinum plated titanium.
(j) Perforated.
(k) Uniform extensive pitting.
(l) Severe pitting.
(m) Severe attack from edge.
(n) Specimens consumed.

*Note:

Exposure	Environment	Temp, F	Test Duration, days
1	55% $CaCl_2$, saturated with NaCl and $CaSO_4$	220	192
2	Partially purified 55% $CaCl_2$	220	29
3	Partially purified 55% $CaCl_2$	220	11
4	62% $CaCl_2$	310	66
5	Partially purified 62% $CaCl_2$	310	11
6	Partially purified 62% $CaCl_2$	310	10
7	73% $CaCl_2$	300	36
8	73% $CaCl_2$	300	43
9	73% $CaCl_2$	300	197
10	Partially purified 73% $CaCl_2$	300	11
11	Partially purified 73% $CaCl_2$	300	10

TABLE 2. EXPOSURES WITH TITANIUM ALLOYS*[3]

Material	Corrosion Rates, mils per year, For Indicated Exposure**								
	1	2	3	4	5	6	7	8	9
Ti	0.002	8[e]	Nil	0.003	0.0006	0.1	> 95[a]	1110	Nil
Alloy 1	Nil	Nil	0.006	0.01	0.0006	0.1	> 90[a]	968[g]	Nil
Alloy 2	0.003	Nil	Nil	0.006	0.001	0.1	2	21.3	0.03
Alloy 3	0.005	Nil	0.01	0.005	0.02	0.9	3	5.6	3
Alloy 4	<1[b]	Nil	Nil	--	0.01	2	--	12.6	--
Alloy 5	2	25[c]	0.003	--	0.02	1	--	>4000[e]	0.6
Alloy 6	Nil	0.03[d]	0.007	0.08	0.03	4	3	--	24
Alloy 7	0.1	14[c]	0.003	0.06	0.02	0.7	>210[a]	>4000[e]	0.3
Alloy 8	Nil	Nil	0.0001	0.02	0.01	0.4	28[f]	223	0.3
Alloy 9	Nil	0.003	--	--	0.02	0.8	--	396	0.4
Alloy 10	Nil	0.03[d]	0.01	0.02	0.02	3	3	14.2	14
Alloy 11	<1[b]	0.02	0.001	0.01	0.02	1	6	33.4	--
Alloy 12	--	Nil	0.01	--	0.05	5	--	10.2[h]	--
Alloy 13	<1[d]	0.02	0.005	--	0.002	--	3	14.4	6

(a) Specimen completely consumed.
(b) One pit in specimen.
(c) Very badly pitted.
(d) Slight attack under spacer.
(e) Perforated.
(f) Scattered pits.
(g) One specimen consumed.
(h) Uniform etch with deep pits.

*Note:

Alloy Compositions

Wrought Titanium				Cast Titanium			
Alloy	Pd	C	Mo	Alloy	Pd	C	Mo
1	0.22	--	--	5	--	1.90	--
2	0.19	0.015	11.90	6	--	1.07	22.66
3	0.20	0.014	19.89	7	--	1.45	--
4	--	0.010	24.62	8	0.20	1.19	--
				9	0.21	1.29	--
				10	0.15	1.30	19.69
				11	0.11	1.16	12.36
				12	--	1.06	29.25
				13	0.17	1.19	20.96

**Note:

Exposure	Environment	Temp, F	Test Duration, days
1	62% $CaCl_2$	310	96
2	73% $CaCl_2$	350	84
3	Wet Cl_2 gas	200	132
4	Cl_2O 15%, wet Cl_2 15%, HOCl, CO_2 40%, air 30%	110	140
5	NaCl brine (chlorine cell anolyte)	200	132
6	62% H_2SO_4, saturated with Cl_2	60	92
7	36% HCl + 200 ppm free Cl_2	Ambient	121
8	31% HCl + 1 ppm free Cl_2, traces chlorinated organics	130	7
9	65% HNO_3 saturated with metal nitrates	210	69

TABLE 3. CORROSION OF TITANIUM WELDS IN SALT SOLUTIONS(5)

Medium	Concentration, wt%	Temperature, F	Mean Corrosion Rate, mpy VT1-1(Unalloyed) Welded Joint	VT1-1(Unalloyed) Parent Metal	OT4(3Al-1.5Mn) Welded Joint	OT4(3Al-1.5Mn) Parent Metal
$MgCl_2$	52-53	325	0.12	0.12	0.02	0.02
$CaCl_2$	50.6	266	0.05	0.05	0	0
NH_4Cl	46.5	239	0.02	0.02	0.04	0.04
		Solution A				
NH_2Cl	18.4	--	--	--	--	--
NaCl	7.9	239	0.02	0.02	0.03	0.03
Na_2SO_4	7.0	--	--	--	--	--

TABLE 4. CORROSION OF UNALLOYED TITANIUM IN VARIOUS SOLUTIONS

Environment	Concentration, percent	Temperature, F	Corrosion Rate, mpy	Reference
$AlCl_3$	10	212	<0.4	(6)
$CaCl_2$	20	212	<3.9	(6)
$CaCl_2$	50.6	266	0.05(a)	(5)
$Ca(ClO)_2$	6	212	<0.04	(6)
CuCl	50	212	<0.04	(4)
$CuCl_2$	10	Boil	<5	(7)
$CuCl_2$	40	212	<3.9	(6)
$FeCl_3$	30	212	<0.4	(6)
$FeCl_3$	50	302	<5	(7)
$HgCl_2$	10	212	<0.4	(6)
$MgCl_2$	52	325	0.12(a)	(5)
NaCl	Saturated	212	<0.4	(6)
NaCl	Saturated	232	<5	(7)
NH_4Cl	46.5	230	0.02(a)	(5)
$SnCl_2$	24	212	<0.04	(6)
NH_4Cl	18.4	239	0.02(a)	(5)
NaCl	7.9	239	0.02(a)	(5)
Na_2SO_4	7.0	239	0.02(a)	(5)
$Al_2(SO_4)_3$	Saturated	75	<5	(8)
Na_2SO_4	10-20	Boil	<5	(8)
$CuSO_4+2H_2SO_4$	Saturated	75	<5	(8)
NH_4ClO_4	15-20	189	<5	(8)
NH_4F	10	75	<50	(8)

(a) Weld and parent metal.

TABLE 5. EFFECT OF pH ON CORROSION OF UNALLOYED TITANIUM IN BOILING 23 PERCENT NaCl(8)

pH	Corrosion Rate, mpy
1.0	33.6
1.1	33.0
1.2	28.0
1.3	25.1
1.4	Nil
1.5	Nil

However, a Ti-0.15Pd alloy was significantly more resistant.(9) Crevice attack, once started, tends to continue even though the crevice is destroyed. Up to 50 percent of exposed crevices show attack in severe environments.(9)

In concentrated salt-refinery brines, the corrosion rate of titanium is reported as about 0.3 mil per year in either standard or alkaline brine. Crevice attack is reported in standard brine (pH 7.5) at 225 F but not in alkaline brine (pH >12) at 208 F. The standard brine contains $CaCl_2$, $MgCl_2$, and NaCl in solution, plus crystals of $CaSO_4$ and NaCl. The alkaline brine contains Na_2SO_4, Na_2CO_3, NaOH, and NaCl plus crystals of NaCl.(10)

The effect of sodium chloride on the pitting tendency of various alloys in H SO has been investigated.(11) The technique employed is to compare standard electrochemical polarization curves for conditions with and without additions of NaCl. Studies in 1N H_2SO_4 at 77 F show almost no increase in the corrosion rate of titanium with addition of 1N NaCl. Hastelloy C shows an increase in current density of up to 10 times for salt addition. Type 316 shows up to 100 times increase and Type 304-L greater than 100 times increase. These data support the view that titanium is more resistant than many other metals to pitting or crevice attack.

Figure 1 indicates areas of temperature and concentration where pitting attack of titanium is reported for calcium chloride and aluminum chloride.(6) The 0.2 palladium-titanium alloy is reported to be resistant to pitting in 73 percent $CaCl_2$ at 350 F.(3,12)

Zinc chloride solutions may also cause pitting attack of titanium.(1)

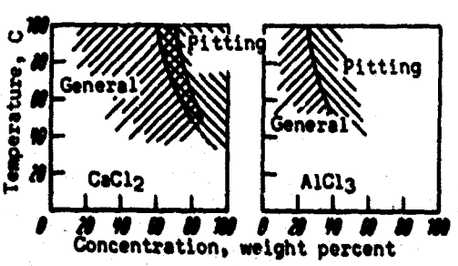

FIGURE 1. TEMPERATURE/CONCENTRATION AREAS FOR PITTING ATTACK OF UNALLOYED TITANIUM IN $CaCl_2$ AND $AlCl_3$(6)

Corrosion Fatigue

Recent studies show the excellent corrosion fatigue behavior of titanium in seawater.(13) Figure 2 compares Ti-6Al-4V with several other materials of construction on a density basis. Table 6 compares the ratio of corrosion fatigue strength to tensile strength for the given materials. The tests were performed by exposing the specimens to seawater without load for 7 days prior to fatigue testing. A Sonntag SF-1-U fatigue machine was operated at 1800 cpm with seawater continuously circulated past the specimen at 2.5 to 3 gallons per minute.

Table 7 gives results of flexural fatigue tests performed in brackish Severn River water

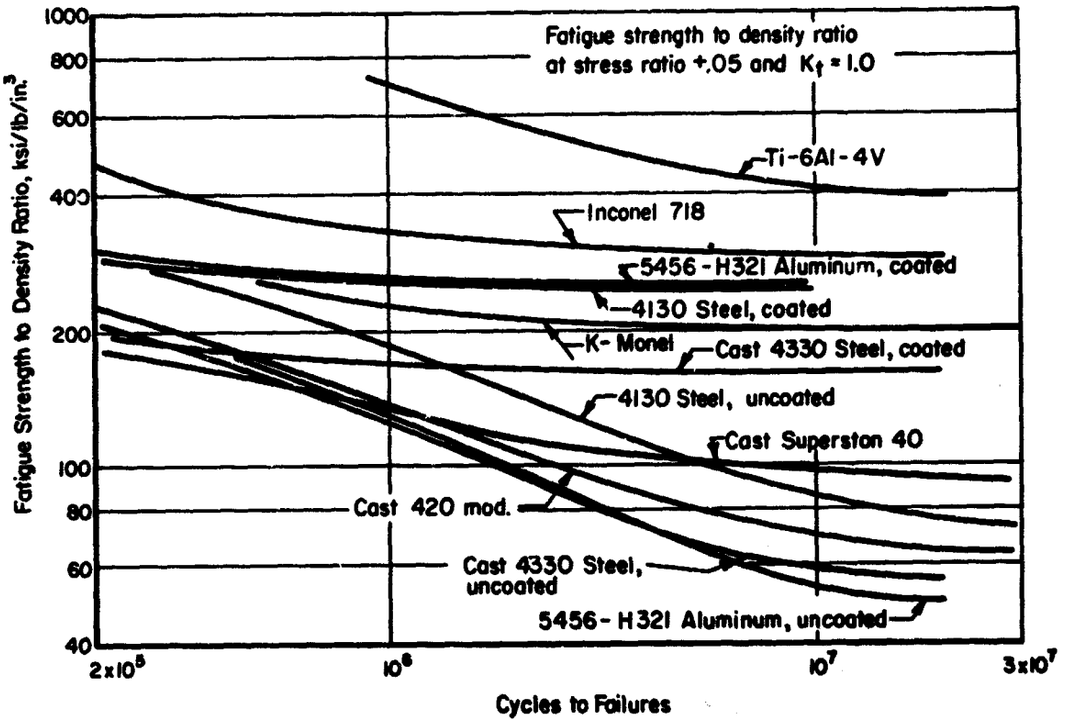

FIGURE 2. CORROSION FATIGUE EFFICIENCY CURVES FOR VARIOUS ALLOYS IN SEAWATER[13]

TABLE 6. CORROSION FATIGUE TO TENSILE STRENGTH RATIOS FOR SEVERAL MATERIALS[13]

Material	Form	F_{tu} Ultimate Tensile Strength, ksi	F_{ec} Corrosion Fatigue Strength at 10^7 Cycles, ksi	Ratio, $\frac{F_{ec}}{F_{ty}}$
Inconel 718	Wrought	181.0	86.8	0.48
Ti-6Al-4V	Wrought	144.5	65.1	0.45
4130 Steel, coated	Wrought	162.7	70.3	0.43
5456-H321 aluminum, coated	Wrought	58.1	24.7	0.43
K-Monel	Wrought	155.4	~61.0	~0.39
Superston 40	Cast	101.4	26.5	0.26
4330 Steel, coated	Cast	180.1	46.0	0.26
4130 Steel, uncoated	Wrought	162.7	24.0	0.15
420 Modified Corrosion Resistant Steel	Cast	134.1	19.9	0.15
5456-H321 Aluminum, uncoated	Wrought	58.1	5.8	0.10
4330 Steel, uncoated	Cast	180.1	15.0	0.08

TABLE 7. RESULTS OF FLEXURAL FATIGUE TESTS AT COMPLETELY REVERSED STRESS[14]

Material	Condition[a]	Fatigue Strength in Severn River Water at 10^8 Cycles, psi
Ti-6Al-4V	W	≈73,000
Ti-6Al-4V	WGPNC Coating	65,000
Ti-4Mn-4Al	W	81,000
Ti-4Mn-4Al	WGPNC Coating	≈60,000

(a) W - wrought; WGPNC - western gear phosphorous-nickel coating.

containing 1/3 to 1/6 the salt content of seawater.[14] It is interesting to note that the nickel-phosphorus coating on titanium decreased its corrosion-fatigue resistance. This coating was employed to decrease the galling and sliding friction of titanium to make it serviceable for use as a propulsion gear in seawater. A contact rolling test was also used to investigate the pitting tendency of the pitch line of gear teeth under load. No pitting was reported but Ti-6Al-4V and Ti-4Mn-4Al with or without the nickel-phosphorus coating was badly worn.

Stress-Corrosion Cracking

Table 8 presents data on studies with Ti-6Al-4V stressed in several salt solutions as well as other media at 75 percent of its yield strength without failures in up to 1800 hours of exposure.[15] In another program, Ti-6Al-4V, Ti-2.5Al-16V, Ti-5Al-2.5Sn, Ti-4Al-3Mo-1V, and Ti-3Al-11Cr-13V were stressed to 75 percent of yield for 1 year without failure in marine atmospheres or tidewater exposures at Kure Beach, North Carolina.[15] Similarly, as noted earlier, Ti-75A, Ti-6Al-4V, Ti-5Al-2.5Sn, and Ti-3Al-11Cr-13V have successfully withstood deep Pacific Ocean exposures through 197 days under stresses from 35 to 75 percent of their yield strength.[4]

Ti-3Al-11Cr-13V stress specimens were evaluated in 1M solutions of NaCl, $NaNO_3$, Na_2SO_4, Na_2PO_3 (all aerated) and Na_2S (nonaerated).[16] No failures were found in 172 days with heat-treated (200,000 psi yield) bent-beam specimens stressed to 75 percent of yield. No failures were found in 230 to 522 days of exposure for U-bend specimens at 140,000 psi yield.

TABLE 8. EXPOSURE OF STRESSED Ti-6Al-4V TO VARIOUS ENVIRONMENTS WITHOUT FAILURE[15]

Environment	Exposure Time, hours[a] Annealed	Heat Treated, Aged	Welded
Aerated tap water	1700	1700	750
Aerated 3% NaCl water	1700	1700	750
Aerated 0.25 percent sodium dichromate solution	1700	1700	750
4 percent soluble oil	1700	1700	750
Trichloroethylene	1150	1150	1150
Cosmoline	1700	1700	750
Laboratory air	--	--	750
Seacoast	1400	1400	1400

(a) Bent-beam tests, specimens stressed to 75 percent of yield strength; yield strength, annealed: 132,000 psi; heat treated and aged: 163,000 psi.

Stress was shown to be detrimental to an alloy containing 5.5 to 6.7 Al and 1.0 to 2.3 Mn in $MgCl_2$ at 374 F, as discussed earlier.[5] With stressed OT4-2 [Ti-(5.5-6.7)Al-(1-2.3)Mn] specimens, cracking developed in the base metal but not in the weldment. This may be due to use of dissimilar (3Al-1.5Mn) weld rod for these welds. In previous studies,[17] the authors showed that increased aluminum contents in titanium alloys gave reduced resistance to cracking when stressed in concentrated nitric acid. Evidently the higher aluminum content of the base metal causes corrosion under stress in $MgCl_2$ at 374 F.

Stress* was not found to be detrimental to any of the three titanium alloys (i.e., VT1-1, OT4, and OT4-2) tested in the solutions shown in Table 3.

Stress-corrosion screening tests were performed in water at 500 F on materials for steam-generator tubing in nuclear power plants.[18] Commercially pure titanium U-bend specimens showed no detrimental attack in the liquid or vapor phase. Although high-purity water was used, 500 to 550 ppm chloride as diluted synthetic seawater and 250 to 350 ppm PO_4 as disodium phosphate were added. The pH was adjusted to 10.6 to 11.2 with NaOH. The oxygen content was 7 to 9 ppm (air saturation at room temperature.

Field Tests

Laboratory and field tests of brine solutions indicate that titanium is an excellent choice for oil-well lift valves when compared with Monel, nickel, J-55, N-80, 9% Ni, and 316 stainless steel.[19] Titanium performed well in laboratory tests using aerated fluids and in field tests of gas lift wells. As shown in Table 9, tests in sour crude wells showed titanium to be inferior to normally used materials. The electrochemical potential of titanium in brine from a Wharton Company Texas well measured by a saturated calomel electrode varied from 0.3471 to 0.3174 volt after 12 minutes.

*Stress levels not disclosed.

TABLE 9. EROSION-CORROSION STUDY OF TITANIUM IN OIL-WELL LABORATORY AND SERVICE TESTS[19]

Environment	Velocity, ft/sec	Exposure Time, days	Corrosion Rate, mpy As Received	Polished
ASTM Brine, air saturated[a]	--	2-3	0.0	--
Crude oil and brine[b]	--	2-5	0.0	--
West Texas crude oil	10	2	0.57	0.28
	40	2	6.7	1.3
3% NaCl + 20 percent West Texas crude oil	10	1-1/4	--	0.0
	40	1-1/4	--	0.26
3% NaCl + 20 percent West Texas crude oil + 1.2 percent 150 to 200 mesh sand	10	1-3/4	--	2.1
	40	1-3/4	--	23
Field Test, crude oil and brine	--	23	--	0.0-0.01

(a) Impingement, 100 psi pressure differential; distance of specimen from 1/64-inch orifice, 1/4, 3/8, and 1-1/2 inches
(b) Impingement, 150 psi pressure differential; distance of specimen from 1/16-inch orifice, 1 inch; from 3/64-inch orifice, 1-1/4 inch.

Field-service testing of titanium shows many areas where titanium should be considered for service. Table 10 gives results of service tests in several chloride solution environments. Note that, while the titanium served well in many of these solutions, it was not serviceable in 350 F 73% $CaCl_2$, NaCl brine with HOCl, or NaCl in chlorine cell orifices.

CORROSION IN MINERAL ACIDS

Sulfuric Acid

General Corrosion

Unalloyed Titanium. Titanium shows poor resistance to sulfuric acid in concentrations greater than about 5 percent. The corrosion rate at room temperature is approximately linear with concentrations up to 20 percent where the penetration is about 30 mils per year.[1] At 40 percent H_2SO_4, the corrosion rate shows a minor peak of about 80 mpy and drops to a minimum at 60 percent acid. A major corrosion peak of up to 600 mpy penetration occurs at 78 percent acid.(see Table 11).[20] In 100 percent acid, the corrosion rate is of the order of 100 mpy. In oleum, the corrosion decreases until a rate of about 10 mpy is reached at 65 percent oleum (SO_3).

At room temperature the corrosion of titanium in H_2SO_4 is slightly lower over the entire concentration range when purged with pure O_2, N_2, or H_2.[20] At elevated temperature, the corrosion rate increases catastrophically when deaerated even at concentrations as low as 1 percent acid.[1] In boiling 1 percent acid, the corrosion rate is 100 mpy or more.[1,22]

The addition of small amounts of some salts to H_2SO_4 solutions decreases the attack of titanium (see Table 12). Note the effect of exposed surface area on the corrosion of titanium.

In the processing of nickel-cobalt ores, titanium is found to be one of the best materials in sulfuric acid solutions containing large amounts of dissolved salts and suspended solids.[25,26,27] The solutions contain 2 to 5 percent free H_2SO_4 with nickel, iron, aluminum, magnesium, and manganese sulfates, in concentrations up to 1 percent by weight each, plus small amounts of cobalt, copper, zinc,

TABLE 10. FIELD TESTING OF TITANIUM EQUIPMENT IN CHLORIDE SOLUTION ENVIRONMENTS(3)

Equipment	Type of Titanium	Environment	Time of Service, months	Remarks
2 inch gate valve	Cast	55% $CaCl_2$ at 220 F	42	Excellent
3 inch schedule 5 pipe	Wrought	55% $CaCl_2$ at 270 to 290 F	8	Excellent
3 inch schedule 5 pipe	Wrought, Ti + 0.2% Pd	55% $CaCl_2$ at 270 to 290 F	8	Excellent
Vertical filter press leaf-wire mesh separation	Wrought	55% $CaCl_2$ at 230 F	9	Excellent
2-inch heating coil	A-55	62% $CaCl_2$ at 310 F	36	One small pit after 1 year. Some pitting above liquor level when test stopped
1/4 inch Thermowell	Wrought	73% $CaCl_2$ at 350 F	9 days	Failed
Nipple	Wrought	Treated filtered 310 gpl NaCl brine	24	Excellent
Heat exchanger	Wrought	310 gpl NaCl brine, pH 4	10	Excellent
Nipples (2)	Wrought	310 gpl NaCl brine, pH 4	10	Excellent
Nipples (6)	Wrought	KCl brine	28	Excellent
Level indicator	Wrought	NaCl brine, pH 2-4	15	Excellent
Bolts on inside flanges of spargers	Wrought	Acid brine	24	Apparently okay
Nipples (8)	Wrought	NaCl brine	10	Excellent
14 inch orifice	A-55	310 gpl NaCl, pH 4	48	Excellent
Orifice	A-70	310 gpl NaCl	48	Excellent
4 inch orifice	Wrought	310 gpl NaCl	36	Excellent
10 inch orifice	A-70	310 gpl NaCl, pH 10-11, 150 to 160 F	48	Excellent
6 inch orifice	A-70	340 gpl KCl	28	Some corrosion and etching at inner edge of gasket
6 inch orifice (2)	A-70	340 gpl KCl, pH 5.2, 160 F	36	Excellent
3 inch orifice	A-70	275 gpl NaCl, pH 1.15	24	Excellent
Orifice	Wrought	Depleted NaCl brine	24	Excellent
Thermowell	A-55	NaCl brine, HOCl, 0.05 to 0.150 gpl, pH 4	48	Excellent
Thermowell	Wrought	NaCl brine, HOCl, 0.05 to 0.150 gpl, pH 4	24	Excellent
Thermowell	Wrought	NaCl brine, HOCl	12	Failed at weld
Thermowell (2)	A-55	300 gpl NaCl, pH 10	48	Excellent
Thermowell	A-55	340 gpl KCl	36	Excellent
Thermowell (2)	A-55	300 to 320 gpl KCl, pH 10 to 10.., 145 to 160 F	36	Excellent
Thermowell	A-55	KCl. 340 gpl, pH 5.2	36	Excellent
Thermowell (3)	Wrought	Acid NaCl brine, pH 2	24	Excellent
Stem on level control	Wrought	NaCl brine	27	Excellent
Chlorine cell feed orifices	Wrought	NaCl brine	3 to 4	Failed in 1 to 2 weeks at one plant, 3 to 4 months at other plant
Titanium electrodes in KCl sump tank	Wrought	Strongly alkaline, weak KOCl solution	18	Excellent

TABLE 11. CORROSION RESISTANCE OF SEVERAL RUSSIAN ALLOYS IN SULFURIC ACID(20,217)

Alloy	Corrosion Rate, mils per year in sulfuric acid, percent								
	10	20	30	40	50	60	70	80	90
Room Temperature									
VT1 (unalloyed)	10	20	--	40	40	25	120	600	120
VT5 (Ti-5Al)	45	70	100	140	--	95	150	570	90
VT3-1 (Ti-4.5Al-2Cr-1Mo)	30	70	--	180	--	--	--	610	150
VT3 (Ti-5Al-2.5Cr)	90	180	210	290	--	25	310	1000	150
44 F									
Unalloyed	--	18	110	200	33	15	130	420	63
Ti-0.1Pd	--	0.8	34	51	43	15	240	340	54
Ti-2Pd	--	Nil	Nil	Nil	0.8	2.3	36	150	64
Ti-1Mo	--	Nil	3.8	29	25	15	87	270	54
Ti-1Mo-0.1Pd	--	Nil	Nil	Nil	1.5	1.5	83	100	40
Ti-1Mo-2Pd	--	Nil	1.5	0.8	1.5	1.5	24	100	41
Ti-15Cr	--	--	130	200	87	11	140	510	77
Ti-15Cr-0.1Pd	--	3.1	4.6	28	37	12	260	330	71
Ti-15Cr-2Pd	--	Nil	Nil	Nil	Nil	0.8	86	25	46
Ti-5Pd	--	Nil	Nil	Nil	0.8	1.5	0.8	95	54

TABLE 12. EFFECT OF ADDITIONS ON CORROSION OF TITANIUM

Acid		Additions		Temperature,	Corrosion,	
Kind	Concentration, percent	Material	Percent	F	mpy	Reference
H_2SO_4	5	Zirconyl sulfate (air saturated)	3 to 4	90	1	(23)
H_2SO_4	45	$Na_2Cr_2O_7$	8	105	0.03	(23)
		Na_2SO_4	8			
		$Cr_2(SO_4)_3$	3			
H_2SO_4	5	$CuSO_4$	0.25, 0.5, 1.0	203	<0.4	(6)
H_2SO_4	5	$CuSO_4$	20	203	3	(6)
H_2SO_4	30	$CuSO_4$	0.25	100	2	(6)
H_2SO_4	30	$CuSO_4$	0.5	100	4	(6)
H_2SO_4	30	$CuSO_4$	1	100	0.8	(6)
H_2SO_4	30	$CuSO_4$	10	100	16	(6)
H_2SO_4	30	$CuSO_4$	0.25	203	3	(6)
H_2SO_4	30	$CuSO_4$	0.5	203	30	(6)
H_2SO_4	30	$CuSO_4$	1	203	30	(6)
H_2SO_4	30	$CuSO_4$	10	203	24	(6)
H_2SO_4	10	$FeSO_4$	2g/1[a]	Boiling	<5[b]	(7)
H_2SO_4	20	Fe^{+++}, Cu^{++}	16g/1	Boiling	<5[b]	(7)
H_2SO_4	17	$FeSO_4$	7 to 8	140	<5	(7)
H_2SO_4	30	$CuSO_4$	1	Boiling	12[c]	(24)
H_2SO_4	30	$CuSO_4$	1	Boiling	62[d]	(24)
HCl	5	--	--	100	13	(6)
HCl	5	$CuSO_4$	0.05	100	1.6	(6)
HCl	5	$CuSO_4$	0.5	100	3.5	(6)
HCl	5	$CuSO_4$	1	100	1.2	(6)
HCl	5	$CuSO_4$	5	100	0.8	(6)
HCl	5	$CuSO_4$	0.05	200	3.5	(6)
HCl	5	$CuSO_4$	0.5	200	2.4	(6)
HCl	5	$CuSO_4$	1	200	2.4	(6)
HCl	10	--	--	100	40	(6)
HCl	10	$CuSO_4$	0.5	100	0.8	(6)
HCl	10	$CuSO_4$	1	100	0.4	(6)
HCl	10	$CuSO_4$	3	100	0.4	(6)
HCl	10	$CuSO_4$	5	100	0.4	(6)
HCl	10	$CuSO_4$	0.5	200	3.9	(6)
HCl	10	$CuSO_4$	1	200	5	(6)
HCl	10	$CuSO_4$	3	200	5	(6)
HCl	10	$CuSO_4$	5	200	5	(6)
HCl	5	CrO_3	0.5	100	0.4	(6)
HCl	5	CrO_3	1	100	0.8	(6)
HCl	5	CrO_3	0.5	200	1.2	(6)
HCl	5	CrO_3	1	200	1.2	(6)
HCl	5	HNO_3	1	100	0.4	(6)
HCl	5	HNO_3	5	100	0.4	(6)
HCl	5	HNO_3	10	100	0.4	(6)
HCl	5	HNO_3	1	200	4	(6)
HCl	5	HNO_3	5	200	4	(6)
HCl	5	HNO_3	10	200	8	(6)
HCl	10	Fe^{+++} impurities	--	Room	<5	(7)
HCl	10	$CuSO_4$	0.05	140	<5[b]	(7)
HCl	10	$CuCl_2$	16g/1	Boiling	<5[b]	(7)
HCl	20	Cu^{++}	0.2g/1	Room	<5[b]	(7)
HCl	37	Cu^{++}	0.2g/1	Room	<5[b]	(7)

(a) Gram per liter.
(b) Greater than 50 mpy in pure acid.
(c) Specimen area 16.08 in.^{2} in about 900 ml solution.
(d) Specimen area 1.32 in.^{2} in about 800 ml solution.

and hexavalent chromium. Above 300 F, titanium is the only metal or alloy found satisfactory. Titanium is also used for valves in 500 F solutions of 1.5 to 2 percent acid, 10 percent dissolved nickel sulfate, and up to 40 percent suspended solids.

The resistance to pitting for titanium exposed to H_2SO_4 containing NaCl is described on page 12.

Titanium Alloys. Most titanium alloys are less resistant to sulfuric acid than unalloyed titanium. The major exceptions are the titanium-noble metal alloys, which are considerably more resistant than unalloyed titanium.[6,7,12,41] Table 13 gives corrosion rates for several alloys in sulfuric acid. Data for several Russian alloys are given in Table 11.

Tables 14 and 15 given corrosion rates of zirconium-titanium and zirconium-titanium-tantalum alloys, respectively. In general, little improvement in corrosion resistance of titanium to sulfuric acid occurs until 50 percent or more zirconium is added.[29] The addition of 5 or 10 percent tantalum to zirconium-titanium (1:1 ratio) gives only slight improvememt in corrosion resistance. Tantalum alloys with up to 40 to 50 percent titanium additions show corrosion rates of less than 5 mpy in boiling 5, 30, or 60 percent H_2SO_4.[30] For the alloy 50Ti-35Ta-15Cb, the corrosion rates in boiling 30 and 60 percent H_2SO_4 were 3 and 8 mils per year, respectively.[30]

The benefit of additions of noble metals to titanium in promoting resistance to H_2SO_4 solutions is shown in Tables 2, 11, 16, 17, 18, and 19.

Galvanic Couples

Tables 20 and 21 give reported corrosion rates for titanium when coupled to a second metal in sulfuric acid. Only coupling of titanium to the noble metals (including iridium, platinum, palladium, and rhodium) is found to reduce the corrosion of titanium to a satisfactory rate in boiling 0.6 and 2N H_2SO_4 (see Table 21).

In helium saturated H_2SO_4, coupling to vanadium reduced the attack on titanium from 3.3 when uncoupled to 0.0 mpy in 95 F, 0.1N H_2SO_4 and from 22 to 0.1 mpy in 95 F, 2N H_2SO_4.[34] Vanadium reduced the rate from 60 to 0.0 mpy in aerated 95 F, 2N H_2SO_4. The corrosion of titanium is nil in aerated 95 F, 0.1N H_2SO_4 coupled or uncoupled.

Anodic Protection

Titanium can be protected during service in sulfuric acid by applying an anodic (positive) potential.[7,35,36] (See Table 22.) A potential of 2.5 to 5 volts reduced the corrosion of titanium from 100 to 1 mpy in 40 percent H_2SO_4 at 140 F. Protection was also maintained in 60 percent acid at 194 F.[36] However, care must be taken to insure that the titanium is completely covered by liquid so that the applied current can reach all areas. In a titanium heat exchanger for hot sulfuric acid service in a rayon process, severe corrosion occurred in the vapor phase of the vessel where the applied current was ineffective.[35]

Stress-Corrosion Cracking

Recent studies have shown that stress has a detrimental effect on the corrosion resistance of a titanium alloy in sulfuric acid, as well as in hydrochloric acid.[37] Unalloyed titanium and Ti-5Al were exposed under stress to sulfuric acid of 7.3 to 70 percent concentration. In Ti-5Al, brittle failure was promoted by small stress at low corrosion rates. Ti-5Al was found to fail brittlely with the formation of a large quantity of cracks along its entire length, in 7.3, 12.9, and 60 percent H_2SO_4 at stresses of up to 102,000 psi (76 percent of the ultimate tensile strength). Microscopic examination showed considerable amounts of hydride precipitate, chiefly along the slip planes, and partially in a direction perpendicular to that of applied external stress. The stress apparently promotes the penetration of hydrogen into the metal, to form hydrides and cause brittle failure.

Hydrochloric Acid

General Corrosion

Unalloyed Titanium. Titanium is severely attacked by HCl except at very low temperature and low concentration. Concentrations much above 5 percent attack titanium even at room temperature. At 150 F, corrosion rates increase rapidly above a concentration of 1 percent, whereas in boiling solutions, even 1 percent HCl rapidly (>100 mpy) attacks titanium.[1,2,22] The addition of certain salts, however, does reduce the attack of HCl on titanium (see Table 12). Similarly, the addition of certain metal ions also reduces the attack of HCl on titanium, as shown in Tables 23, 24, and 25. Figure 3 compares the effect of metal-ion concentration on the change of the corrosion potential of titanium. Note that a concentration of copper of more than 10^{-3} moles per liter greatly increases the potential of titanium, thus lowering its corrosion. Copper is known to be an effective inhibitor in HCl solutions.

Titanium Alloys. In general, alloys of titanium show the same or reduced resistance to HCl, as shown in Table 13. However, several noble-metal alloys of titanium, such as palladium, platinum, and molybdenum, have considerable resistance to HCl in rather severe conditions of temperature and concentration (see Tables 2, 16, 17, 19, and 26). Tantalum additions also increase the HCl resistance of titanium.[30] For instance, a binary Ti-25Ta alloy has a corrosion rate of only 2 mil per year in boiling 3 percent acid. In boiling 20 percent acid, an addition of 50 percent tantalum or more is required for similar resistance.

However, some Ti-Ta alloys became brittle after exposure to HCl.[30] This embrittlement was greatly alleviated by contact with small areas of noble metals, or by addition of 0.2 to 0.5 platinum to the alloy. An alloy of 15 percent columbium, 35 percent tantalum, and 50 percent titanium alloy had a corrosion rate of about 5

TABLE 13. CORROSION RESISTANCE OF TITANIUM ALLOYS[28]

Alloy	Corrosion, mils per year: 95 F Air Agitation, H_2SO_4 5%	95 F Air Agitation, HCl 3%	95 F Air Agitation, HCl 5%	95 F N_2 Agitation, H_2SO_4 5%	95 F N_2 Agitation, HCl 3%	95 F N_2 Agitation, HCl 5%	190 F, No Agitation, H_2SO_4 5%	190 F, No Agitation, HCl 1%	190 F, No Agitation, HCl 3%
Ti (75 BHN)[a]	56	0.07	--	16	4.9	16	450	0.1	140
Ti (120 BHN)	(b)	0.17	--	20	5.2	8	250	3.3	140
Ti (180 BHN)	10	0.03	--	18	5.1	10	570	0.2	200
Ti (200 BHN)	8	0.07	--	31	6.4	11	560	0.1	220
Ti-8Mn (annealed)	17	0.13	29	42	9	18	880	0.3	230
Ti-6Al-4V (annealed)	45	1.4	32	32	12	19	870	60	360
Ti-6Al-4V (aged)	27	4.1	27	30	8	16	850	49	380
Ti-5Al-2.5Sn (annealed)	44	14	37	53	23	39	1230	83	590
Ti-8Al-2Cb-1Ta (annealed)	37	0.5	15	24	10	17	650	1.5	310
Ti-2.5Al-16V (solution treated)	0.7	0.5	5	21	5.5	10	590	3.4	160
Ti-2.5Al-16V (aged)	24	0.2	14	38	9	18	660	3.7	211
Ti-1Al-8V-5Fe (annealed)	(b)	0.06	--	44	13	20	890	37	430
Ti-1Al-8V-5Fe (aged)	(b)	0.3	--	46	15	22	950	74	450
Ti-3Al-2.5V (annealed)	(b)	0.1	0.05	16	5	7.4	670	0.3	150

(a) BHN = Brinell hardness number.
(b) Erratic.

TABLE 14. CORROSION RESISTANCE OF ZIRCONIUM-TITANIUM ALLOYS IN SULFURIC ACID[29]

Alloy Zr	Alloy Ti	Corrosion Rate, mils per year[a]: 68 F 40%	68 F 75%	68 F 94%	104 F 5%	104 F 10%	104 F 20%	104 F 40%	104 F 60%	104 F 75%	140 F 40%	212 F 5%	212 F 10%	212 F 40%	212 F 75%
100	--	Nil	Nil	590	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	0.4	Nil	Nil
95	5	Nil	Nil	1200	Nil	Nil	Nil	Nil	Nil	0.5	Nil	Nil	0.3	Nil	70
90	10	Nil	190	1100	Nil	Nil	Nil	Nil	--	55	Nil	Nil	2.7	16	210
80	20	Nil	270	990	0.9	Nil	0.6	Nil	105	--	Nil	1.1	2.3	45	--
70	30	Nil	230	460	0.9	Nil	0.6	Nil	--	--	18	4	5	200	--
60	40	Nil	360	520	0.8	3	1.2	22	--	--	67	12	36	--	--
50	50	4	700	600	1.3	1.9	1.3	60	410	--	200	38	38	--	--
40	60	13	650	410	2.3	20	0.7	60	260	--	350	27	110	--	--
30	70	34	700	190	7	34	81	95	160	--	430	41	100	--	--
20	80	35	810	155	7	35	78	440	134	--	920	35	350	--	--
10	90	95	820	72	11	110	220	570	105	--	1400	51	710	--	--
5	95	105	780	64	15	--	--	810	80	--	1160	280	830	--	--
--	100	126	730	61	12	15	490	950	54	--	2000	950	1070	--	--

(a) Based on reported weight losses and estimated alloy densities.

TABLE 15. CORROSION RESISTANCE OF ZIRCONIUM-TITANIUM-TANTALUM ALLOYS IN SULFURIC ACID[29]

Alloy Zr	Alloy Ti	Alloy Ta	Corrosion Rate, mils per year[a]: 104 F 5%	104 F 10%	104 F 20%	104 F 60%	140 F 40%	212 F 5%	212 F 10%	212 F 40%
50	50	--	1.3	1.9	1.3	700	200	38	38	415
47.5	47.5	5	0.6	0.6	1.1	170	130	11	--	890
45	45	10	0.5	1.0	1.0	--	150	10	0.4	460

(a) Based on reported weight losses and estimated alloy densities.

TABLE 16. EFFECT OF PALLADIUM ADDITION ON CORROSION OF TITANIUM IN ACID[6]

Material	Temperature, F	Corrosion Rate, mils per year: H_2SO_4 5%	H_2SO_4 10%	H_2SO_4 25%	HCl 1%	HCl 3%	HCl 5%	HCl 10%
Titanium	100	32	40	80	--	--	--	--
Titanium	140	--	--	--	0.8	35	60	160
Ti + 0.15Pd	140	0.6	0.8	7.5	Nil	0.1	0.2	2

TABLE 17. EFFECT OF VARIOUS ALLOY ADDITIONS ON CORROSION RESISTANCE OF TITANIUM[31]

Composition	Weight Loss in 24 Hr,[a] mil/yr: Boiling H_2SO_4 1%	Boiling H_2SO_4 10%	Boiling HCl 3%	Boiling HCl 10%
Titanium	460	3950	242	4500
Ti + 0.064% Pt	<2	145	<2	128
Ti + 0.54% Pt	<2	48	3	120
Ti + 0.08% Pd	<2	166	3	100
Ti + 0.44% Pd	<2	45	<2	67
Ti + 0.1% Rh	<2	26	5	96
Ti + 0.5% Rh	3	48	<2	55
Ti + 0.1% Ru	3	187	5	280
Ti + 0.5% Ru	<2	48	<2	113
Ti + 0.11% Ir	<2	359	3	120
Ti + 0.60% Ir	<2	45	3	88
Ti + 0.10% Os	5	480	3	1820
Ti + 0.48% Os	<2	82	3	208
Ti + 0.11% Re	235	--	345	--
Ti + 0.36% Re	9	--	30	--
Ti ± 0.11% Au	1050	--	1500	--
Ti + 0.48% Au	3	--	9	146
Ti + 0.04% Ag	500	--	334	--
Ti + 0.34% Ag	--	--	--	4850
Ti + 0.17% Cu	470	--	340	--
Ti + 0.44% Cu	660	--	550	--

(a) The possible weighing error of these tests is ±2 mil/yr.

TABLE 18. EFFECT OF O_2 AND H_2 ON CORROSION RESISTANCE OF TITANIUM AND TITANIUM ALLOYS IN ROOM TEMPERATURE 20 PERCENT H_2SO_4[31]

Alloy	Gas	Weight Loss, mil/yr
Titanium	O_2	4[a]
	H_2	29
Ti + 0.37% Pt	O_2	<2[b]
	H_2	<2
Ti + 0.44% Pd	O_2	<2
	H_2	<2

(a) Passive during most of test.
(b) The possible weighing error of these tests is ±2 mil/yr.

TABLE 19. EFFECT OF Pt AND Pd ALLOY ADDITIONS ON THE CORROSION RESISTANCE OF TITANIUM IN OXYGEN-FREE H_2SO_4 AND HCl AT 190 C (374 F)[31]

Composition	Weight Loss,[a] mil/yr: H_2SO_4 1%	H_2SO_4 5%	H_2SO_4 10%	H_2SO_4 20%	HCl 3%	HCl 5%	HCl 10%
Titanium	515	--	--	--	2250	--	--
Ti + 0.03% Pt	<2	<2	3.4	Diss	--	--	--
Ti + 0.29% Pt	<2	<2	3.3	11.5	<2	<2	890
Ti + 0.08% Pd	<2	<2	3.5	Diss	--	--	--
Ti + 0.44% Pd	<2	<2	5.0	12.0	<2	<2	1120

(a) One-period tests, 44 to 64 hr duration. The possible weighing error in these tests is ±2 mil/yr.

TABLE 20. GALVANIC COUPLING OF TITANIUM TO VARIOUS CATHODIC MATERIALS IN BOILING H_2SO_4[32]

Couple	Area Ratio, Ti to Cathode	Corrosion Rate, mpy: Boiling 1% H_2SO_4	Boiling 3% H_2SO_4 + 5% Na_2SO_4	Boiling 5% H_2SO_4 + 5% Na_2SO_4
Ti	--	450	580	930
Ti-18-8	1	0	--	--
	2	3	--	--
	6.6	2	--	--
Ti-Hast F	1	0	--	--
	12	0.6	--	--
Ti-C	0.2	0	0	1150
	0.5	--	0	--
	1	--	380	--
Ti-Pt	0.25	--	--	6.7
	1	--	--	21
	2	--	--	21
	4	--	--	35
	35	--	--	540

TABLE 21. CORROSION RATES, MILS PER YEAR, OF TITANIUM IN BOILING H_2SO_4 AND HCl WHEN COUPLED TO VARIOUS METALS[33]

Coupling Metal	0.6M H_2SO_4	Coupling Metal	2M H_2SO_4	Coupling Metal	2M HCl
Ag	2300 to 10,000	Ni	1940	Sb	2200
V	2300	Pd	1820	V	2000
Au	2100	Au	1790	Cu	1970
Cu	2070	Cu	1790	Ag	1970
Sb	1750	Fe	1670		
Fe	1620	Ag	1590	Pb	1340
				Sn	1180
Ni	1400	Rh	1270	Fe	1150
Co	1400	Pt	1110	In	990
Pb	1180	In	1100		
Pd	1150			Co	840
Sn	1020	Pb	840	Bi	820
		Bi	810	Cd	800
Bi	960	Sn	800	Al	740
Cd	860			Ni	660
Zn	830	Ir	0		
Hg	770			Au	110
Rh	0			Pd	0
Pt	0			Rh	0
Ir	0			Pt	0
				Ir	0

TABLE 22. RESISTANCE OF TITANIUM TO REDUCING ACIDS WITH CONTINUOUS ANODIC PASSIVATION(7)

Acid w/w percent	Temperature, F	Potential Versus H_2 Scale, volts	Corrosion Rate With Applied Potential, mpy	Factor by Which Rate of Corrosion is Reduced
40% Sulphuric Acid	140	2.1	<5	11,000
40% Sulphuric Acid	194	1.4	<5	996
60% Sulphuric Acid	140	1.7	<5	662
60% Sulphuric Acid	194	3.0	<5	163
80% Sulphuric Acid	140	1.0	<50	140
37% Hydrochloric Acid, conc	140	1.7	<5	2,080
60% Phosphoric Acid	140	2.7	<5	307
60% Phosphoric Acid	194	2.0	<50	100
50% Formic Acid	BP	1.4	<5	70
25% Oxalic Acid	194	1.6	<5	1,000
25% Oxalic Acid	BP	1.6	<50	350
20% Sulphamic Acid	194	0.7	<5	2,710

TABLE 23. CORROSION RATE OF TITANIUM IN 15% HCl WITH Pt, Cu, AND Fe IONS(38)

Solution	Cations Added	Concentration of Additive, gm-ions/l x 10^{-6}	Corrosion Rate, mpy
15% HCl	None	--	18
	Fe^{3+}	40	19
		50	22
		80	0
	Cu^{2+}	5	19
		10	25
		20	30
		30	24
		40	0
	Pt^{4+}	0.5	42
		0.75	51
		1	45
		2	0
15% HCl + 0.8% NaF	None	--	226
	Pt^{4+}	0.5	23,600
		15	24,700
		50	25,000

TABLE 24. EFFECT OF METAL CATIONS AT 10^{-3}M ON THE CORROSION OF TITANIUM IN BOILING 2M HCl(33)

Metal	Corrosion Rate, mpy
Iron	680
Cobalt	1000
Nickel	1500
Copper	1300
Silver	800
Cadmium	800
Tin	920
Rhodium	Nil
Palladium	Nil
Antimony	Nil
Iridium	Nil
Platinum	Nil
Gold	Nil
Lead	840

TABLE 25. EFFECT OF FOUR-VALENT TITANIUM ON CORROSION RATES OF UNALLOYED TITANIUM IN VARIOUS SOLUTIONS(8)

Solution	Ti^{+4} Concentration,(a) grams/liter	Temperature	Corrosion Rate, mpy
15% H_2SO_4 + 4% $CuSO_4$	0.11	Boiling	About 20
	0.44		0.9
	0.66		Nil (positive weight gain)
10% HCl	0.5	Boiling	Spec. dissolved
10% HCl	1.0		Nil (positive weight gain)
20% HCl	2.88		Spec. dissolved
20% HCl	5.76		Nil (positive weight gain)
1% HCl + 5% HNO_3	0	Boiling	2.9
	0.03		0.4
	0.43		Nil (positive weight gain)
2% HF	0	Room	6520
	50		1970
	100		Nil (positive weight gain)

(a) A Ti^{+4} ion as such is not considered to exist in aqueous solution.

TABLE 26. CORROSION RESISTANCE OF TITANIUM ALLOYS IN HCl[21]

	Corrosion in HCl, mils per year							
	Boiling			64 F				
Alloy	1%	3%	5%	15%	20%	25%	30%	35%
Titanium	410	1870	3400	70	200	480	740	1310
Ti-0.1Pd	50	180	390	0.8	19	40	90	1210
Ti-2Pd	12	--	40	Nil	Nil	1.5	4	400
Ti-15Mo	50	180	500	Nil	Nil	100	120	410
Ti-15Mo-0.1Pd	30	50	60	Nil	Nil	Nil	20	80
Ti-15Mo-2Pd	9	--	17	Nil	Nil	Nil	Nil	1.5
Ti-15Cr	330	1530	2600	34	100	370	650	990
Ti-15Cr-0.1Pd	30	70	110	3	4	20	26	180
Ti-15Cr-2Pd	6	--	9	Nil	Nil	Nil	4	30
Ti-5Pd	--	--	--	Nil	Nil	1.5	15	800

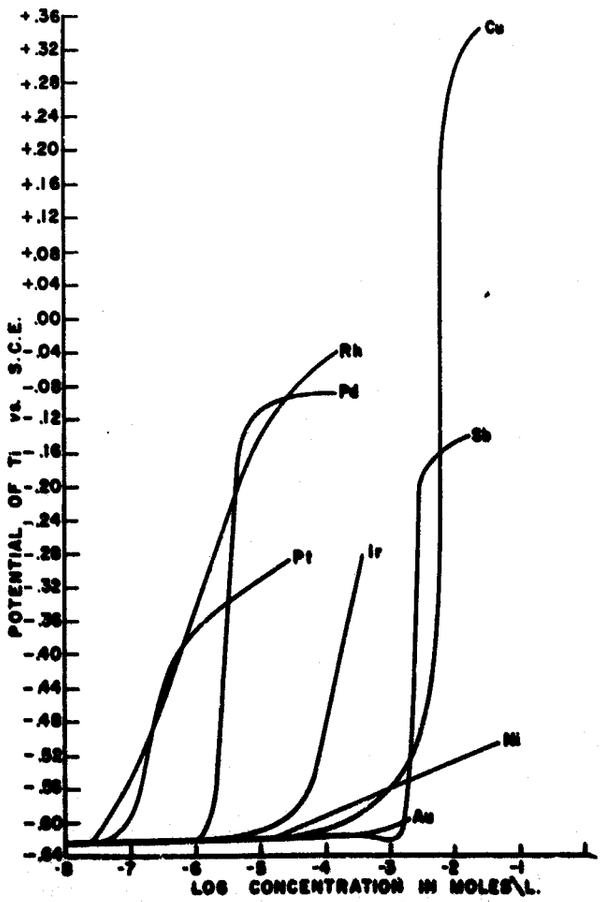

FIGURE 3. THE EFFECTS OF EIGHT METALLIC CATIONS ON THE POTENTIAL OF A TITANIUM SAMPLE IN BOILING 2M HYDROCHLORIC ACID[33]

mil per year in boiling 20 percent HCl. Substitution of more than 15 percent columbium for tantalum caused a rapid increase in the rate of attack.

Galvanic Couples

The corrosion of titanium in boiling 2M HCl when coupled to various metals is shown in Table 21. Only the noble metals reduce the attack on titanium to a reasonable level.

Anodic Protection

Titanium can be protected in HCl solutions by suitable anodic currents.[7,36] For example, anodic protection of titanium is possible in 37 percent HCl at 140 F (see Table 22).

Stress-Corrosion Cracking

Titanium has been known to be susceptible to stress-corrosion cracking in 10 percent HCl. Failure was reported for Ti-5Al-2.5Sn stressed to 90 percent of the proportional limit in 95 F acid, (see reference 39). Recent studies have shown that a Ti-5Al alloy suffers brittle failure in 5, 3 and 10 percent HCl (as well as H_2SO_4 solutions).[37] Both VT-1 (unalloyed titanium) and VT5 (Ti-5Al), welded and unwelded, were exposed to HCl solutions at various stress levels. The time to failure was found to vary with the stress level, as shown in Figure 4.

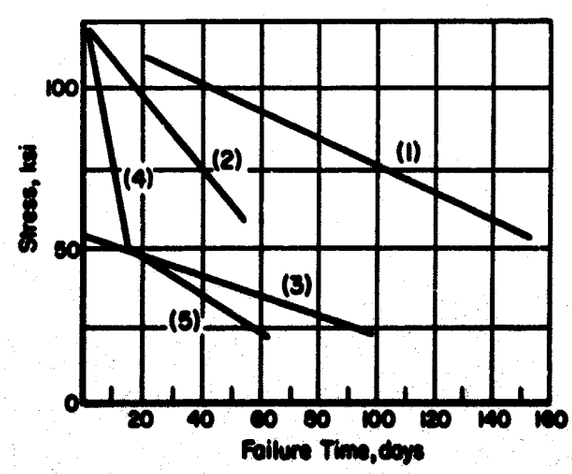

FIGURE 4. EFFECT OF STRESS ON TIME TO FAILURE OF UNALLOYED TITANIUM AND Ti-5Al IN HCl SOLUTIONS[37]

(1) Ti-5Al in 5 percent HCl.
(2) Ti-5Al in 10 percent HCl
(3) Unalloyed Ti in 10 percent HCl
(4) Welded Ti-5Al in 10 percent HCl
(5) Welded Ti in 10 percent HCl.

Brittle failure occurred in Ti-5Al and was promoted by small stresses and low speed of corrosion. Cracks were formed on Ti-5Al in 5.3 percent HCl at stresses as high as 102,000 psi (76 percent of the ultimate tensile strength). Microscopic examination showed a solid greyish blue hydride layer.

It is believed that stress on the Ti-5Al alloy promoted the penetration into the metal during exposure to HCl solutions. The precipitation of titanium hydrides then occurred chiefly along the slip planes and partially in the direction perpendicular to the applied stress. Failure then resulted in a brittle manner. Welded samples failed more quickly.

Field Tests

Titanium nuts and bolts show good resistance in a variety of hydrochloric acid fumes, as shown in Table 27.

Other Halogen Acids

Titanium is attacked very rapidly by hydrofluoric acid, even in low concentrations (see Reference 2).

No attack on titanium is reported in boiling 10 percent hydriodic acid and little attack is indicated in various concentrations of hydrogen bromide at high temperature.[1]

Nitric Acid

General Corrosion

Titanium is quite resistant to nitric acid at all concentrations and up to the boiling point. Titanium heating coils are used commercially for 70 percent acid at boiling.[40] Under the heat-transfer conditions used here, titanium was more resistant than many of the other metals tested except zirconium[41] (see Table 28).

The resistance of titanium to chemical attack is believed to be related to the precipitation of tetravalent titanium, Ti^{+4}, to form a protective TiO_2 film on the surface.[24,8] Thus, even in highly oxidizing boiling 70 percent nitric acid, the corrosion rate of titanium decreases with time and with increasing ratio of area of titanium to volume of acid (see Table 29).

The effect of temperature on the nitric acid resistance of titanium is shown in Table 30. Note that the corrosion seems to reach a minimum at a temperature near 480 F. However, a considerable variation in corrosion rates was noted with change in sample area to acid volume ratio,[22] as previously discussed.

A titanium +0.15 percent palladium alloy is reported to have about the same corrosion resistance as unalloyed titanium at the boiling point in 20, 50, and 65 percent nitric acid.[6] The corrosion rates of titanium-zirconium alloys in 98 percent nitric acid at 212 F are shown in Table 31. Alloys of titanium with 20 and 30 percent molybdenum have poor resistance to nitric acid.[6] Corrosion rates of 150 to 500 mil per year would be expected in boiling 15 and 60 percent acid.

The corrosion of several titanium alloys with palladium, molybdenum, and carbon in hot 65 percent acid saturated with metal nitrates is shown in Table 32.

Stress-Corrosion Cracking

As noted above and in Reference 2, titanium has low corrosion rates in both white and red fuming nitric acid.* 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.

Phosphoric Acid

Titanium shows behavior in phosphoric acid similar to its behavior in hydrochloric acid. However, its passive range extends to about 30 percent H_3PO_4 at room temperature.[1] Titanium corrodes less than 1 mpy in 30 percent acid at 95 F, 5 percent acid at 140 F, and 1 percent acid at 212 F.[2] At the boiling point, titanium is rapidly attacked even in dilute acid (10 mpy in 1 percent acid.[22]

Table 33 gives corrosion data for zirconium-titanium alloys in phosphoric acid.

Titanium can be anodically protected in 60 percent acid at 140 F (see Table 22). Table 34 compares the corrosion resistance of titanium, zirconium, and titanium-zirconium alloys at various applied potentials in H_3PO_4 and HNO_3 mixtures.

Mixed Acids

Titanium shows good resistance to mixed oxidizing acids. Table 35 presents data for mixtures of HNO_3-H_2SO_4.

In a boiling solution (about 230 F) of 2M HCl-5M HNO_3, titanium shows excellent resistance.[42] This solution is used in a nuclear fuel recovery process known as "Darex" for dilute aqua regia. Even with actively dissolving Type 304 stainless steel, the corrosion rate of Ti-45A and Ti-6Al-4V is less than 0.2 mpy.

In the "Zircex" process (for dissolution of zirconium-clad fuel elements), titanium showed little attack in laboratory studies with boiling 0.5M HNO_3 + 0.4M UCl_2 or 3M HNO_3 + 0.4M UCl_3.[42] Titanium is attacked in another step of the process; that of boiling azeotropic (6.1M) hydrochloric acid. Bubbling of nitrogen dioxide through the solution reduced the attack of titanium to a very low rate in both the liquid and the vapor phase. Chlorine gas reduced the attack similarly, but only in the vapor phase. Nitrous oxide, nitric oxide, and nitrosyl chloride give no inhibition.[42]

* Military Specification:
White fuming HNO_3 - 97 percent Min HNO_3, 0 to 0.015 percent NO_2, 2 percent Max H_2O.
Red fuming HNO_3 - 82 to 85 percent HNO_3, 14 ± 1 percent NO_2, 2.5 ± 0.5 percent H_2O.

TABLE 27. FIELD TESTING OF TITANIUM EQUIPMENT IN HYDRYCHLORIC ACID ATMOSPHERE[3]

Equipment	Type of Titanium	Environment	Time in Service, months	Remarks
Nuts and bolts on manhole cover on hydrochloric acid tank car	Wrought	HCl fumes and spillage	30	Excellent
Nuts and bolts, muriatic acid absorber system	A-70	HCl fumes	40	Excellent
Capscrews for securing seal on muriatic acid loading pump	Wrought	HCl fumes and spillage	15	Excellent
Bolts for securing seals to muriatic acid loading pump	Wrought	HCl fumes and spillage	36	Excellent

TABLE 28. VAPOR-LIQUID CORROSION OF VARIOUS ALLOYS IN 65% HNO_3 USING PRESSURIZED INTERFACE HEAT TRANSFER UNIT[41]

Metal	Gauge Press	Heat Flux Immersion		Heat Flux[e] 1/2 Immersion		Cooling[e] 1/2 Immersion		Control Immersion		Control Vapor	
		Temperature, C	MPY	Temperature, C	MPY	Temperature, C	MPY	Temperature, C	MPY	Temperature, C	MPY
321 SS	4.5	138	107	140	142	122	21	127	23	126	23
304 SS	15.0[a]	160	3,400	170	3,350	143	569	151	2,370	—	303
309 SS	15.0[a]	162	107	176	106	142	34	149	64	—	25
310 SS	8.5	147	33	146	47	126	11	135	14	133	13
Inconel	6.0[b]	152	9,800	153	10,700	126	78	135	18,100	131	1,100
Multimet	6.5	142	36	143	42	124	17	129	17	127	23
Haynes Alloy 25	15.0	156	149	160	115	132	67	141	72	136	86
Hastelloy Alloy C	7.5[a]	168	4,500	147	2,400	129	863	135	2,600	118	408
Titanium	30.0[c]	201	2	225	2	170	15	181	2	174	1
Zirconium	30.0[d]	171	<1[f]	179	<1[f]	142	<1[f]	155	<1[f]	147	<1[f]

(a) Estimated pressure.
(b) 18 hour exposure.
(c) 48 hour exposure.
(d) 72 hour exposure.
(e) Temperature reported is for liquid phase area of specimen, vapor phase temperatures run 2 to 10 C hotter.
(f) Actually <0.1 mpy.

TABLE 29. VARIATION OF CORROSION OF UNALLOYED TITANIUM IN BOILING 70% HNO_3 WITH EXPOSED AREA AND LENGTH OF EXPOSURE[8,24]

Sample Area to Solution Volume, sq in./liter	Exposure Period, hr	Corrosion Rate, mils/yr
0.5 and 5	<1	46
	20	18
	340	Nil
130	<1	6
	20	0.5
	340	Nil

TABLE 30. CORROSION RATES OF TITANIUM IN NITRIC ACID AT HIGHER TEMPERATURE(6,22)

Temperature, F	Corrosion Rate, mil/yr, at Indicated Concentration, percent									Reference
	5	10	20	30	40	50	60	70	98	
95	0.06	0.2	0.4	0.2	--	--	--	--	0.08	(6)
212	0.6	1.4	1.4	0.2	--	0.2	--	0.8	--	(6)
Boiling (212 to 250 F)	--	--	5	8	15	30	23	14	--	(22)
374	--	--	--	80	110	110	50	15	--	(22)
392	--	--	--	--	26	--	--	--	--	(6)
482	--	<1	<1	<1	<1	<1	<1	<1	--	(22)
554	--	--	14	--	--	--	--	45	--	(6)

TABLE 31. CORROSION RESISTANCE OF ZIRCONIUM-TITANIUM ALLOYS IN 98 PERCENT SOLUTIONS OF NITRIC ACID AT 212 F(29)

Alloy Composition, percent		Corrosion Rate, mpy
Zr	Ti	
100	--	Nil
95	5	Nil
90	10	Nil
80	20	4.5
70	30	12
60	40	12
50	50	13
40	60	9.3
30	70	34
20	80	35
10	90	1.5
5	95	0.8
--	100	0.8

TABLE 32. CORROSION OF TITANIUM ALLOYS IN 65 PERCENT HNO_3 AT 210 F, SATURATED IN METAL NITRATES(3)

Alloy Content, percent			Corrosion Rate, mpy
Pd	C	Mo	
--	--	--	Nil
0.22	--	--	Nil
0.19	0.015	11.90	0.03
0.20	0.014	19.89	3
--	1.90	--	0.6
--	1.07	22.66	24
--	1.45	--	0.3
0.20	1.19	--	0.3
0.21	1.29	--	0.4
0.15	1.30	19.69	14
0.17	1.19	20.96	6

TABLE 33. CORROSION RESISTANCE OF ZIRCONIUM-TITANIUM ALLOYS IN PHOSPHORIC ACID(29)

Alloy		Corrosion Rate, mils per year(a)									
		68 F				104 F				212 F	
Zr	Ti	20%	40%	60%	80%	20%	40%	60%	80%	20%	40%
100	--	Nil	Nil	Nil	1.6	Nil	0.3	16	21	Nil	1.1
95	5	Nil	Nil	0.5	4	Nil	1.1	22	16	Nil	2.7
90	10	Nil	Nil	1.1	2.2	Nil	1.1	8	22	11	110
80	20	Nil	1.1	2.8	9	0.5	11	11	51	23	110
70	30	Nil	1.8	4	12	1.2	18	29	82	60	180
60	40	0.4	3.6	6	12	4	36	43	90	43	360
50	50	1.9	4	6	13	6	50	50	95	13	570
40	60	2.0	7	7	13	7	47	47	100	20	930
30	70	1.4	5	7	10	14	40	41	75	70	950
20	80	1.4	3.5	7	11	14	49	49	85	210	990
10	90	1.5	2.2	2.9	4	7	37	22	37	510	1030
--	100	0.7	2.3	2.3	3	3.8	31	23	46	610	1300

(a) Based on reported weight losses and estimated alloy densities.

TABLE 34. CORROSION RESISTANCE OF TITANIUM, ZIRCONIUM AND ZIRCONIUM-TITANIUM ALLOYS IN PHOSPHORIC AND NITRIC ACID MIXTURES AT DEFINITE POTENTIALS(29)

Solution		Potential	Corrosion Rate, mpy		
H_3PO_4, percent	HNO_3, percent	NH, v	Zr	Ti	50%Zr-50%Ti Alloy
88	--	-0.2	gain	1600	840
88	0.25	+0.1	79	1100	255
88	0.5	+0.4	0	250	110
88	5.0	+0.7	gain	0	gain

TABLE 35. CORROSION OF TITANIUM IN MIXTURES OF NITRIC AND SULFURIC ACIDS[6]

Concentration, percent		Corrosion, mpy	
HNO_3	H_2SO_4	95 F	150 F
100	0	0.3	0.1
90	10	0.3	0.5
50	50	1.4	16
20	80	10	80
10	90	10	10
5	95	3	80
0	100	230	400

A comparison of several metals and alloys in various fuel-processing systems is shown in Table 36.

Titanium has also been examined for use in the Zirflex process for zirconium dissolution.[44] Solutions of 16M nitric acid with additions of 1M HF, 1M HF + 1M Cr, 1M HF + 0.2M Cr, 0.1M HF + 1M Cr, or 1.8M + 0.52M Cr were studied. Even the least corrosive solution (listed in descending corrosiveness) attacked titanium at a rate of more than 1 inch per year. However, with the addition of zirconium, in an amount 1/3 to 1/2 that of the fluoride, the corrosion rate of titanium could be reduced to the order of 1 mil per year.[44]

Effect of Radiation

In-pile exposure of titanium has been reported in several environments. In general, the corrosion of titanium increases with an increase in radiation flux. In the case of hydrochloric acid, however, exposure to alpha activity results in lowered corrosion rates because of production of hydrogen peroxide in the liquid phase and O_3 in the vapor phase[45] (see Table 37).

In-pile studies were performed using solutions containing 0.4M H_2SO_4 (about 4 percent) + 0.17M UO_2SO_4 + 0.15M $CuSO_4$. Corrosion of Ti-55A varied from 0.7 mpy at a flux of 4.3 watts/ml to 1.5 mpy at 16.9 watts/ml. Ti-6Al-4V corroded at about twice the rate of Ti-55A at similar power densities.[46] In similar studies, the corrosion rate of Ti-5Al-2.5Sn was reported as 1.4 mpy at 20 watts/ml.[47]

High radiation fluxes were found to increase the rate of oxide-film formation on titanium specimens.[48] The studies were performed in 10 percent O_2-argon atmosphere at 68 F, 1 atmosphere pressure, at a radiation of 90 x 10^6 rad (cobalt 60, gamma) and neutron flux of 10^{12} n/cm^2.

CORROSION IN GASES

Chlorine

Titanium is rapidly and almost explosively attacked in dry chlorine gas, even at room temperature. In the presence of moisture (>0.013 percent), however, titanium is almost completely resistant to chlorine.[7,49] This critical water content may be as low as 50 ppm.[50] Exposures of titanium to various chlorine-containing environments are described in Tables 2, 38, 39, and 40. Titanium is presently being used for wet chlorine heat exchangers and coolers.[8,51]

Titanium is reported to be susceptible to crevice attack under some conditions in moist chlorine.[50,52] Crevice corrosion was found under Teflon tape in a chlorine duct at 190 F. A blue corrosion product believed to be Ti_2O_3 was found, which subsequently turned white when exposed to air. The mechanism is believed to be a slow dehydration below the critical moisture level in stagnant crevices having a large metal to gas ratio. The reaction rate then increases due to the accumulation of acidic hygroscopic corrosion products.[53]

Hydrogen

In general, the reactivity of titanium with hydrogen follows the same pattern as that observed for titanium with such other reactive gases as oxygen and nitrogen. Under certain conditions, all three of these gases can react with and seriously embrittle titanium and its alloys. The degree of reaction with these gases is a function of time, temperature, and pressure.

A discussion of the effects of hydrogen on the properties of titanium and its alloys is beyond the scope of this memorandum. Nonetheless, it can be stated that, in general, the absorption by titanium of hydrogen in amounts above about 90 to 150 ppm can result in hydride precipitation, embrittlement, and subsequent failure under stress. Certain alloying additions, including aluminum and such beta stabilizers as vanadium and molybdenum, increase the tolerance of titanium for hydrogen considerably. The Ti-6Al-4V alloy, for example, is quite resistant to hydrogen embrittlement and loss of ductility rarely occurs with less than 300 ppm hydrogen.

The high reactivity of titanium with gaseous hydrogen at moderate-to-high temperatures has been known and accepted for some time. At the other temperature extreme, titanium has been found to be completely passive in liquid hydrogen. The temperature regime of reactivity which is of greatest concern is that which extends from room temperature to about 800 F where the behavior of titanium and its alloys has been erratic.

In brief, a review of the available DMIC data shows that the reactivity of titanium and its alloys with hydrogen can be broken down roughly into three temperature regimes which are defined as follows:

Temperature Range, F	Extent of Hydrogen Reactivity
-423 to -300	No evidence of reaction
70 to 800	Erratic behavior; reactions sometimes observed with subsequent property degradation
840 and above	Rapid reaction and subsequent loss of ductility.

Table 41 summarizes the time, temperature, and pressure data on which the above summary tabulation is based. Some details from the studies which have been conducted in the lower temperature ranges of interest are discussed in the paragraphs which follow.

TABLE 36. COMPARISON OF MATERIALS IN FUEL-RECOVERY SYSTEMS[43]

Alloy	Darex[a]		Zirflex[b]		Thorex[c]		UO_2[d] Dissolvent		Sulfex[e]	
	Exposure, hr	Rate, mils/mo	Exposure, hr	Rate, mils/mo	Exposure, hr	Rate, mils/mo	Exposure, hr	Rate, mils/mo	Exposure, hr	Rate, mils/mo
Titanium-45A	674	0.01	672	6.06	672	0.03	528-336	9-11.1	672	0.04
Hastelloy C	674	0.36	672	0.01	672	0.33	336	5.2	672	0.06
Hastelloy F	674	0.05	672	0.04	672	0.03	840	0.69	672	0.01
L/SNA	506	57.3	504	0.01	672	0.03	840	0.27	672	0.08
Carpenter 20 SMb	506	6.71	504	0.03	672	0.03	840	0.48	672	0.02

(a) Darex decladding solution: 45 g of 304 stainless steel and 5 g of Type 302B stainless steel dissolved in 1 liter of 2M 2M HCl-5M HNO_3.
(b) Zirflex decladding solution: 25 g of zirconium dissolved in 1 liter of 6M NH_4F-1.0M NH_4NO_3.
(c) Thorex solution: 375 g of 96% ThO_2-4%UO_2 pellets dissolved in 1 liter of 13M HNO_3-0.04M $Al(NO_3)_3$-0.04M NaF.
(d) UO_2 core dissolvent: 453 g of UO_2 dissolved in 1 liter of 10M HNO_3 containing 0.01M Zr^{4+} and 0.05M NaF.
(e) Sulfex solution: 30 g of Type 304 stainless steel dissolved in 1 liter of 4M H_2SO_4-0.001M NaF.

TABLE 37. EFFECT OF HIGH ALPHA RADIATION ON THE CORROSION OF TITANIUM[45]

Solution	Temperature, C	Corrosion Rates, mpy		Exposure, hr	Comments
		Vapor	Solution		
6M HCl-20 g/l La	45	143	441	20	Very heavy attack
		91	405	164	
	105	2250	4990	18	Catastrophic
		Dissolved	Dissolved	133	
6M HCl-20 g/l Am	45	(a)	3.1	22	No evidence of corrosion
		(a)	3.5	156	
	105	1430	4870	20	Test terminated
10M LiCl-0.5M HCl-20 g/l La	45	63	217	24	Acid depleted
		13	51	166	
	110	900	700	41	Test terminated
10M LiCl-0.5M HCl-20 g/l Am	45	(a)	(a)	19	No evidence of corrosion
		0.3	1.4	131	
	110	(a)	1.0	19	
		(a)	0.9	160	

(a) Slight weight gain.

TABLE 38. EXPOSURES IN GASEOUS CHLORINE(3)

Material	Corrosion Rate, mils per year, For Indicated Exposure*						
	1(i)	2(i)	3(j)	4	5	6	7
Ti(a)	(e)	(e)	—	0.009	0.0006	0.003	(e)
Ti(b)	—	—	—	—	Nil	—	—
Ti(c)	—	—	—	—	Nil	—	—
Ti(d)	—	—	—	—	0.02	—	—
Zr	(e)	(e)	0.04	>55(g)	—	13(g)	(e)
Monel	0.01(f)	0.1	0.04	—	—	>27(e)	—
Hastelloy C	0.002	0.01	—	12.8(h)	—	13(g)	0.04
Duriron	—	—	—	—	—	—	3.8
Durichlor	—	—	—	—	—	—	2.6
Chlorimet 3	Nil	0.01	—	85(h)	—	2.5	0.03
Stainless 316	(e)	0.65	0.05	—	—	—	—
Carpenter 20	—	—	—	—	—	—	0.4
Mild Steel	0.1	1.8	0.1	—	—	—	—

*Note:

Exposure	Environment	Temperature, F	Duration of Test, days
1	Dry Cl_2 gas	90	126
2	Dry Cl_2 gas	77	251
3	Dry Cl_2 gas	90	99
4	Wet Cl_2 gas	60	166
5	Wet Cl_2 gas	200	192
6	Wet Cl_2 gas with some seawater spray	104	300
7	Cl_2 gas with entrained 88.1% sulfuric acid and organic impurities	140	166

(a) Regular titanium.
(b) Powder metallurgy titanium - 95 to 99 percent density.
(c) Powder metallurgy titanium - 95 to 99 percent density.
(d) Powder metallurgy titanium - 95 to 99 percent density.
(e) Specimens completely consumed.
(f) Data for one specimen, other specimen damaged.
(g) Perforated.
(h) Metal gone under spacer.
(i) The titanium specimens apparently ignited, destroying or damaging adjacent specimens.
(j) Repeat of exposure No. 1, without titanium.

TABLE 39. EXPOSURE IN SOLUTIONS CONTAINING FREE CHLORINE(3)

Material	Corrosion Rates, mils per year, For Indicated Exposure*				
	1	2	3	4	5
Ti(a)	0.0008	Nil	Nil	30	38.7(d)
Ti(b)	--	--	--	10	--
Zr	(c)	--	--	2(e)	15
Ta	--	--	--	0.02	--
Duriron	--	1.4	0.06	--	0.2(e)
Durichlor	--	2	0.2	--	0.2(e)
Chlorimet 3	8.3	--	--	--	1.3
Hastelloy C	1.9	8.9	1.8	--	0.8
Worthite	--	0.02	0.1	--	--
Carpenter 20	--	--	--	--	0.5(f)
Stainless 316	--	Nil	0.04	--	--

(a) Regular titanium.
(b) Platinum plated titanium.
(c) Specimens consumed.
(d) Specimens perforated.
(e) Scattered pitting.
(f) Attack under spacer.

*Note:

Exposure	Environment	Temperature, F	Test Duration, days
1	H_2O saturated with Cl_2	205	166
2	4 gpl ClO_2 solution	60	1.7
3	4 gpl ClO_2 solution	60	15
4	36% HCl with 200 ppm free Cl_2	Ambient	143
5	70% H_2SO_4 saturated with Cl_2	60	102

TABLE 40. FIELD TESTING OF TITANIUM EQUIPMENT IN CHLORINE ENVIRONMENTS(3)

Equipment	Type of Titanium	Environment	Time in Service, months	Remarks
2 inch gate valve	Cast	17% HOCl	36	Excellent
1 inch cooling coil	A-55	HOCl neutralizer tank	36	Excellent, replaces silver
2 inch Y valve	Wrought	45% H_2SO_4 saturated with Cl_2	30	Excellent
3/4 inch butterfly valve shafts	A-70	Wet Cl_2 gas, 185 F	36	Excellent
Spray drier atomizer wheel	Wrought	18% Ca $(OCl)_2$ solution	60	Excellent, replaces Hastelloy C
1 inch diaphragm valve	Cast	Chlorinated NaCl brine	36	Excellent
1/4 inch steam tracer tubing	Wrought	HCl and Cl_2 fumes	30	Excellent
Heat exchanger	Wrought	ClO_2 and steam at 212 F	14	Excellent
Chlorine contact cooler sparger pipes	Wrought	Chlorinated hot water, hot, wet Cl_2 gas	48	Excellent
Pump impeller	Cast	Depleted NaCl brine saturated with Cl_2	24	Excellent
Pump	Cast	Nearly saturated NaCl brine, containing 100 to 150 ppm Cl_2	12	Excellent
Sparger pipe and distributor bolts	A-70	Depleted NaCl brine, Cl_2 0.008 gpl	30	Excellent
1/4 inch straps on sparger pipes	A-70	Depleted NaCl brine, Cl_2 0.008 gpl	30	Excellent
Level-trol	Wrought	Depleted NaCl brine, wet Cl_2 vapors	36	Excellent
10 inch orifice	A-70	Acid NaCl brine, Cl_2 0.4 gpl	48	Excellent
3 inch orifice	A-70	NaOH 7%, NaOCl 25 gpl, 100 F	24	Excellent
Thermowell	A-55	NaCl 275 gpl, Cl_2 0.2 to 0.5 gpl	48	Excellent
Thermowells (2)	A-55	KCl 300 to 320 gpl, Cl_2 100 to 150 ppm	36	Excellent
Thermowell	Wrought	NaOH 7%, NaOCl 2%, 100 F	9	Excellent
Diaphragm cell top liner	Sheet	Wet Cl_2 gas and NaCl brine, 200 F	15	Failed at welds
Stud bolts	A-70	Chlorine plant atmosphere	42	Excellent
Thermowell	Wrought	Wet Cl_2 gas	51	Excellent
18 inch butterfly valve	Wrought	Wet Cl_2 gas	18	Excellent
1 inch diameter shaft for 10 inch butterfly valve	Wrought	Acid chlorine contaminated air	54	Excellent
Thermowells (6)	Wrought	Wet Cl_2 gas at 82 F	12	Excellent
Butterfly valve stem	Wrought	Wet Cl_2 gas	9	Apparently okay
Thermowells (7)	Wrought	Cl_2 gas and Cl_2 saturated H_2O at 200 F	9	Excellent
Packing support grid and sparger tube	Wrought	Alkaline NaOCl	36	Excellent
Pump shaft sleeve	Wrought	Chlorinated NaCl brine	1	Failed by pitting under rubber sleeve
Heat exchangers, 1220 sq ft (2)	Wrought	Sodium chlorate cell liquor, 110 F	6	Excellent
Heat exchanger, 15 sq ft	Wrought	Sodium chlorate cell liquor, 70 to 100 F	9	Excellent

TABLE 41. SELECTED DATA ILLUSTRATING THE REACTIVITY OF TITANIUM AND TITANIUM ALLOYS WITH HYDROGEN

Material	Temperature, F	Pressure	Time	Remarks	Reference
Unalloyed Ti	75	1 atm	--	H_2 absorbed	(54)
	75	52,000 psi	60 days	No embrittlement observed	(55)
	75 to 140	300 psi	5 to 250 hr	Surface hydride formed; erratic behavior	(56)
	900	1 atm	10 min	RT embrittlement observed	(57)
Ti-5Al-2.5Sn	-423	--	1/2 to 5 hr	No effect on RT tensile or fatigue properties	(58)
	-423	--	100 hr	No effect on RT creep properties	(59)
	400 to 600	1 atm	4 hr	No RT bend embrittlement	(57)
	800 to 2400	1 atm	4 hr	RT bend embrittlement	(57)
	212	2 atm	8 months	No H_2 absorbed, stressed or unstressed	(60)
	450	2 atm	4 months	Unstressed - no H_2 absorbed Stressed - H_2 absorbed	(60)
	840	2 atm	1 month	H_2 absorbed, stressed and unstressed	(60)
Ti-5Al-2.5Sn (ELI)	-423 to -300	0 to 300 psia	918 hr	No H_2 absorbed	(56)
	-423 to 70	0 to 300 psia	556 hr	No H_2 absorbed	(56)
	70 to 140	300 psi	5 to 250 hr	Surface hydride formed; erratic behabior	(56)
	400 to 800	1 to 15 psia	5 to 100 hr	Erratic H_2 absorption	(61,62)
Ti-6Al-4V	-423	--	1/2 to 5 hr	No effect on RT tensile or fatigue properties	(58)
Ti-4Al-4Mn	212	2 atm	8 months	H_2 absorbed, stressed and unstressed	(60)
	450	2 atm	4 months	H_2 absorbed, stressed and unstressed	(60)
	840	2 atm	1 month	H_2 absorbed, stressed and unstressed	(60)
Ti-8Mn	75	52,000 psi	60 days	No embrittlement observed	(55)

Cryogenic Temperatures

To the knowledge of DMIC, no evidence exists which indicates any reactivity of titanium or its alloys with liquid hydrogen. Liquid hydrogen is, for the most part, noncorrosive, and alloys such as Ti-5Al-2.5Sn have found successful application as containers for liquid hydrogen in a number of aerospace applications. For example, as a part of one such vendor qualification program, hydrogen analyses and bend tests were performed on two Ti-5Al-2.5Sn ELI alloy tanks which received exposures to liquid hydrogen and supercritical gaseous hydrogen for times to 918 hours.[56] Table 42 lists the exposure conditions and the environmentally induced stresses on these tanks, and Table 43 shows the results of hydrogen analyses performed on samples from both tanks. It was noted that, while the welds contained slightly more hydrogen than the tank halves, all hydrogen values were well under the 200-ppm maximum allowed by specifications for this material. Bend tests were also performed on samples cut from these two tanks and tested to examine the inner tank surface ductility. The results showed all samples met the minimum specified 8T bend and did not "otherwise indicate embrittlement".

Also, several other investigators have performed various mechanical property tests on titanium alloys after exposure to liquid hydrogen which indicated the compatability of these materials. Specifically, Favor, et al,[58] showed that neither the yield strength nor fatigue limits of the Ti-5Al-2.5Sn or Ti-6Al-4V alloys were significantly affected after continuous exposure of from 1/2 to 5 hours in liquid hydrogen. Also, creep tests performed on the Ti-5Al-2.5Sn alloy, stressed to 85 to 90 percent of its room-temperature yield strength for exposure times to 100 hours in liquid hydrogen, failed to show any evidence of embrittlement by hydrogen.[59]

70 to 800 F

As indicated in Table 41, the reactivity of titanium and its alloys with hydrogen in this temperature range has been extremely erratic, especially at ambient temperatures. The factors which appear to promote reaction at these temperatures include a clean surface, stress, high-purity gas, the presence of beta-phase in the alloy, an acicular microstructure, and, of course, increased temperature and pressure.

TABLE 42. HYDROGEN EXPOSURE OF Ti-5Al-2.5Sn (ELI) ALLOY DURING QUALIFICATION TESTS[56]

	Tank A	Tank B
Age	150 hr at -423 to -300 F, 300 psia	150 hr at -423 to -300 F, 300 psia
Servicing	150 hr at -423 to -300 F, 0 to 300 psia	100 hr at -423 to 70 F, 14.7 psia
Vibration	150 hr at -423 to -300 F, 0 to 300 psia	100 hr at -423 to -300 F, 0 to 300 psia
Operation	468 hr at -423 to -300 F, 210 to 300 psia	206 hr at -423 to -300 F, 210 to 300 psia
Total	918 hr	556 hr

TABLE 43. GAS ANALYSIS OF EXPOSED Ti-5Al-2.5Sn ELI TANKS[56]

Identification	Hydrogen Content, ppm
Tank A (918 hr)	
1st half	60
2nd half	64
Weld bead	84
Tank B (556 hr)	
1st half	58
2nd half	66
Weld bead	92
Requirement	200 max

Previous work has shown that titanium will react with gaseous hydrogen at ambient temperature under certain conditions. Gibb and Kruschwitz found that titanium reacted rapidly with hydrogen at 70 F if high-purity gas was in contact with clean metal.[54] In this work, iodide titanium was precleaned by heating in vacuum at 1830 F to adsorb any surface films. These authors also reported that traces of oxygen or nitrogen, and possibly other gases, in the hydrogen greatly retarded the reaction rate. Similar conclusions were reported by Stout and Gibbons in their studies of the use of titanium as a getter.[63] In their work, also, it was found that a small layer of surface oxide effectively blocked the reaction. Stout and Gibbons precleaned their material by annealing in vacuum at 2100 F. Both of these studies involved hydrogen pressure of less than 1 atmosphere.

Later work by Hughes and Lamborn[64] showed that hydrogen contamination does not occur when titanium is exposed to moisture below about 1100 F. This was attributed either to suppression of the breakdown of water by titanium below this temperature or to the formation of a protective oxide, or oxygen-rich surface layer, at low temperature. The latter explanation is favored by the observation that an oxide scale or oxygen-rich surface layer retards hydrogen pickup by titanium.[65]

Alloy composition affects the reaction between titanium and hydrogen, as would be anticipated, in view of the greater solubility and diffusion rate of hydrogen in beta titanium than in alpha titanium. Savage found significant reaction at 210 F between Ti-4Al-4Mn alloy and hydrogen at 2-atm pressure but little reaction with Ti-5Al-2.5Sn.[60] No special techniques were used in this study to clean either the alloys or the gas. Stressed samples appeared to react more rapidly than unstressed samples. In a study of acid pickling of titanium, McKinsey, Stern, and Perkins,[6] found that unalloyed titanium formed surface hydrides which were reasonably stable at 70 F. Small amounts of beta in alpha titanium tended to cause increased absorption of the hydrogen in the metal. This was particularly noticeable when the material was heat treated so as to produce an acicular structure. For example, a Ti-Fe alloy containing only 2 percent retained beta absorbed twice as much hydrogen as unalloyed titanium when heat treated to give an equiaxed alpha structure, and over three times as much hydrogen when heat treated to produce a coarse acicular structure. Much of the hydrogen was present as surface hydrides in all cases.

In the period of July, 1962, to July, 1963, General Dynamics/Convair (formerly Astronautics) undertook a study to select and evaluate optimum materials for application in liquid hydrogen-liquid oxygen fueled, recoverable aerospace vehicles. A part of this study was concerned with a determination of the effects of hydrogen exposures at elevated temperatures on the mechanical properties of the Ti-5Al-2.5Sn ELI alloy. The results of this study are detailed in Reference 61 and are summarized in the conclusions to that study which are quoted as follows:

"Long-time (100-hour) thermal exposures at 400, 600, and 800 F in various pressure of hydrogen gas resulted in significant decreases in notched tensile strength and crack-propagation properties at -423 F. However, a more severe exposure occurred as a result of applying a mechanical load during thermal exposures at 600 F in various pressures of hydrogen gas. The application of the load caused failure in nearly half of the notched tensile specimens during exposure. The poor creep-rupture life during 600 F exposure and the decrease in toughness resulting from these exposures is believed to be due to hydrogen absorption. Microstructural studies substantiated this deficiency by showing the formation of large numbers of titanium hydride platelets. The decrease in toughness and the poor creep-rupture life caused by exposure to hydrogen gas is felt to be a serious problem. For this reason it is recommended that additional studies be performed to more accurately define the effects of hydrogen exposures on the Ti-5Al-2.5Sn ELI alloy before it is used structurally in an elevated-temperature hydrogen environment."

The above experiences were later rechecked[62] with additional 75 and -423 F tests on sheets of the Ti-5Al-2.5Sn ELI alloy. A total of more than 900 specimens were exposed under conditions where temperatures ranged from 200 to 800 F; applied loads ranged from 0 to 50,000 psi; gas pressures ranged from 1 to 15 psig of hydrogen, hydrogen-helium, and hydrogen-helium-water vapor mixtures; and times ranged from 5 to 64 hours. The test specimens included tensile, notched tensile, and fusion-weld tensile specimens which were tested at 75 and -423 F

after exposure. Three heats of the Ti-5Al-2.5Sn ELI alloy in four gages (0.006, 0.013, 0.017, and 0.032 inch) were evaluated. The hydrogen gas used contained 1.5 percent nitrogen, 0.13 percent oxygen, 8 ppm water, and the balance hydrogen. The results of this later study are quoted in summary as follows:

"The most significant result of this investigation is that there was little or no effect of the hydrogen exposures on the mechanical properties of the Ti-5Al-2.5Sn ELI alloy. This is true regardless of heat number, sheet thickness, or exposure condition (i.e., temperature from 200 to 800 F, applied loads from 0 to 50,000 psi, exposure times from 5 to 64 hours, gas pressures from 1.0 to 15.0 psig, and various gas exposures including pure hydrogen and hydrogen-helium or hydrogen-helium-water-vapor mixtures). In the previous study (Reference 61), there were significant decreases in strength properties as a result of hydrogen exposures at elevated temperatures (at 400, 600, and 800 F). For example, notched tensile strengths at -423 F decreased from 10 to 20 percent, depending upon exposure conditions, as a result of the hydrogen exposures. In this investigation the largest effects ranged from a 6 percent increase (in room temperature tensile strength) to a 5 percent decrease (in notched tensile strength at 423 F after an 800 F exposure). These differences are very nearly within the margin of testing error (based on an average obtained from three replicate specimens). It is therefore concluded that there was little or no effect of hydrogen exposures on the mechanical properties of the Ti-5Al-2.5Sn ELI sheet material."

These results were obviously not consistent with those of the previous program described earlier.[61] Because of these inconsistencies, the more recent study[62] concluded with the suggestion that additional test data be obtained to substantiate or negate the data that were obtained.

In the opinion of DMIC, it appears possible that the differences in results from these two programs may be due to differences in the purity of the hydrogen gas used. Unfortunately, no analyses were reported for the gas used in the initial work, although ample evidence was reported that the hydrogen had, under certain exposure conditions, reacted with the titanium alloy. On the other hand, the hydrogen used in the follow-up work was relatively impure and, in fact, may have contained sufficient impurities to completely suppress reaction with the titanium alloy. At any rate, these experiences point up the need for special precautions in both securing a source of high-purity hydrogen and maintaining a clean metal surface in order to quantitatively assess the extent of titanium-hydrogen reactions at low pressures and temperatures.

Along similar lines, DMIC has also received a report of sporadic surface hydride formation and occasional embrittlement in tubing of unalloyed (Grade A40) and the Ti-5Al-2.5Sn ELI alloy exposed to gaseous hydrogen at temperatures to 140 F and pressures to 300 psi for times of 5 to 250 hours.[56] Here, the hydriding reaction appeared to occur most rapidly in the heat-affected zones of welds in these tubing materials and was greatly accelerated in welds which had been contaminated during welding. This reaction also tended to occur more readily with the unalloyed titanium than with the Ti-5Al-2.5Sn ELI alloy.

In view of these experiences, it is recommended that the use of titanium in contact with pressurized hydrogen gas at ambient temperatures be examined quite carefully.

Permeability

The permeability of titanium to hydrogen has been estimated at elevated temperature,[67] (see Table 44). At temperatures of 500 to 800 F, the absorption of hydrogen can become appreciable and embrittlement would normally be expected. These numbers are only estimates, since the actual diffusion of hydrogen into the metal is dependent on the permeability of the surface films as well as a number of other factors noted in the preceding section of this memorandum.

TABLE 44. CALCULATED PERMEATION INTO A VACUUM OF 0.040-INCH-THICK METAL TO HYDROGEN AT ONE ATMOSPHERE[67]

Material	Temperature, F	Permeability Constant, P(2)	Hydrogen Loss J, cc/cm²-sec
Palladium	800	8.4×10^{-3}	6.3×10^{-1}
Titanium	800	—	2.3×10^{-2}
Iron	800	1.8×10^{-6}	1.4×10^{-4}
Nickel	800	1.0×10^{-6}	7.6×10^{-5}
Copper	800	1.6×10^{-8}	1.2×10^{-6}
Aluminum	800	1.0×10^{-9}	7.6×10^{-8}
Titanium	500	—	6.0×10^{-5}
Titanium	100	—	4.5×10^{-12}

Note: Based on the procedure outlined in Jost,[68] the extrapolated data for the diffusion coefficient from Albrecht and Mallett,[69] and the hydrogen solubility reported in TML (now DMIC) Report 100,[70] the hydrogen permeation through titanium can be calculated. Thus, the maximum permeation of hydrogen through alpha titanium would be

4.5×10^{-12} cc H_2/cm^2-sec at 100 F
6×10^{-4} cc H_2/cm^2-sec at 500 F
2.3×10^{-2} cc H_2/cm^2-sec at 800 F.

Other

Titanium is resistant to hydrogen sulfide and sulfur dioxide.[1,7] Corrosion rates of less than 5 mpy are reported.[1] In a recent application, a titanium cooling tower was constructed for cleaning and cooling sulfur dioxide and sulfur trioxide gases.[7]

Titanium panels exposed above a Naval Station boiler stack showed no attack at 572 F in a mixture of hydrogen, carbon monoxide, and carbon dioxide.[1]

Titanium is considered resistant to ammonia and finds use in ammonia stills for the Solvay soda ash process[51] and ammonia synthesis compressors.[36]

DESCALING TITANIUM

A recent evaluation of descaling procedures for titanium has been reported.[71] Both acid solutions and fused alkali baths have been studied in an attempt to eliminate the use of hydrofluoric acid solutions. The results are summarized in Table 45. The effectiveness of etching mill scale from titanium in the acid etchants was found to be dependent on the oxidation temperature. The scale that forms at 1470 to 1560 F is much denser and more chemically resistant to acid. It is difficult to detach the scale satisfactorily without overpickling the metal itself. The scale that forms above 1830 F is removed easily in acid solutions.

TABLE 45. DESCALING OF TITANIUM[71]

Medium	Exposure, min	Temperature, F	Metal Lost by Overpickling, g/meter^2
15% H_2SO_4 + 3% NaF	30	104	240
15% HCl + 3% NaF	25	86	270
8% HNO_3 + 3% NaF	35	104	255
Fused NaOH	15	806	12.7
Fused 80% NaOH + 20% $NaNO_3$	25	932	44.8

The alkali melts were found to satisfactorily pickle titanium without excessive overpickling (metal loss). Sodium hydroxide was especially effective. A "finish" pickle consisting of washing in hot 15 percent H_2SO_4 is recommended.

CORROSION IN ORGANIC COMPOUNDS

Food

Titanium performs well in certain troublesome food processing areas, for example, pickels, catsup, and other tomato products, pineapple juice, relishes, and onion soup.[8] Food also has less tendency to stick to titanium than to other metals.

Methyl Alcohol Solutions

General Corrosion

Studies have shown that solutions of methyl alcohol with additions of bromine are extremely corrosive to titanium and titanium alloys.[72] Corrosion data are presented in Table 46. 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 46, 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.

The corrosion rate of titanium is substantially lowered by additions of water to methyl alcohol-bromine solutions. See Table 47. 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.

TABLE 46. CORROSION OF SEVERAL RUSSIAN ALLOYS IN METHYL ALCOHOL-BROMINE SOLUTIONS[72]

Alloy[a]	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[b]					
VT1	19	11	5	4	3

(a) Iodide, VT1 and VT5 are alpha alloys. VT3 and VT3-1 are alpha-beta alloys.
(b) Increase in ohmic resistance divided by weight loss of the specimen.

TABLE 47. EFFECT OF WATER ON CORROSION OF VT1 UNALLOYED TITANIUM IN METHYL ALCOHOL-2 PERCENT BROMINE SOLUTIONS[72]

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

(a) Increase in ohmic resistance divided by weight loss of the specimen.

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.

Stress Corrosion Cracking[a]

Titanium (as well as zirconium) has been found to suffer stress-corrosion cracking in methanol containing HCl or H_2SO_4.[73] 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.

(a) As this memorandum went to press, preliminary data were received by DMIC from NASA which showed that the solution-treated-and-aged Ti-6Al-4V alloy is susceptible to some form of stress-corrosion cracking in reagent grade methanol. Details of these experiences will be summarized in a forthcoming DMIC technical note.

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 found in the HCl solution.[73]

Other Organic Chemicals

Titanium performs well in many organic chemicals. See Reference 1 or 2 for further discussion. Organic compounds which do attack titanium are usually moderately strong reducing agents, such as formic or oxalic acids. Titanium is generally resistant to other organic acids (see Table 48).

In formic acid, titanium has borderline passivity in solutions of more than 10 percent acid. If aeration is maintained, it may be resistant to higher concentrations at temperatures above room temperature. Table 49 presents corrosion data for some titanium alloys. The addition of 0.15 percent palladium to titanium decreases its corrosion in boiling 50 percent formic acid from >50 to <5 mils per year.[7]

Titanium can be anodically protected in boiling deaerated 50 percent formic acid[7,36] (see Table 22). The anodic polarization of titanium at high voltages up to 50 volts is described in Reference 74. A form of localized attack described as "micropitting" is reported at concentrations of 0.1 to 60 percent formic acid to 104 F at potentials above 12 to 14 V. Uniform corrosion occurs above 96.5 percent acid. A passive area is reported at temperatures above 120 F.

Titanium shows poor resistance to oxalic acid. Data on certain alloys are shown in Table 48. The addition of 50 percent or more tantalum to titanium reduces the attack of 1 percent boiling oxalic acid from a very high rate to less than 5 mpy.[30] The addition of 8, 16, or 35 percent columbium to a 50 percent titanium alloy, remainder tantalum, gave corrosion rates of about 20 mpy in boiling 1 percent acid.[30]

Anodic polarization of titanium is reported in 25 percent oxalic acid at 194 F to boiling[7,36] (see Table 22).

Titanium is used commercially in several applications involving organic chemicals. For example, a titanium pump impeller has replaced Hastelloy C in a solution of 3 percent ethylene chlorohydrin plus 6 percent HCl plus slugs of free chlorine at 140 F. No attack was found after 4 years.[75] In the production of acetaldehyde from ethylene, titanium is used for piping, pumps, valves, heat exchangers, and lines for vessels up to 32 x 10 feet.[52,8] Titanium is also used for various equipment for urea synthesis.[8] A titanium impeller on a tank agitator has shown good service in acid chlorobenzene plus ferric chloride.[3]

Titanium is resistant to process streams in the production of tall oil.[76] Exposure in distillation columns, fractionating towers, and reboiler vapor nozzles shows no change of titanium specimens after up to 5800 hours of tests. Conditions vary from vapors of 93 percent tall oil fatty acids plus 4 to 5 percent rosin acids at 425 F to 90 to 93 percent linoleic-oleic acids plus steam at 475 F with velocity of 62 feet per second and to tall oil vapor with 75 to 80 percent rosin at 510 F.

Autoclave tests have shown that polyphenyls used as heat-transfer media are corrosive at 700 F to aluminum, zirconium, and their alloys, and slightly corrosive to mild steel and tantalum. Only stainless steels are unattacked, but titanium, tungsten, and molybdenum do quite well.[77]

Many organic compounds are effectively adsorbed on titanium surfaces.[8] In this manner, many behave as corrosion inhibitors; for example, m- and p-nitroaniline, p-nitrophenol, 2,4 dinitrophenol, nitrobenzene, and o-nitroanisole are described as effective inhibitors for titanium in 5N H_2SO_4. Nitrobenzene, o-nitrotoluene, 1-nitrobutane, o-nitrochlorobenzene, p-nitrophenol, and o-nitrophenol are effective inhibitors of titanium in HCl. This protection is probably due to a monolayer of the protective organic compound adsorbed onto the titanium or outer TiO_2 surface.

Limited studies, summarized in Table 10, indicated that the application of stress had no effect on the corrosion behavior of the Ti-6Al-4V alloy in trichloroethylene, cosmoline, or a 4 percent soluble oil.[15]

STRESS-CORROSION CRACKING IN NITROGEN TETROXIDE

Recent experiences have shown that the Ti-6Al-4V alloy is susceptible to stress-corrosion cracking in some grades of nitrogen tetroxide, N_2O_4. Previously, titanium and its alloys were believed to be compatible with N_2O_4. In the absence of stress, titanium shows almost no corrosion in liquid or gaseous N_2O_4 in tests to 165 F.[78] Although titanium is impact sensitive at high impact levels,[79] no propagation of the reaction is reported.

Stress-Corrosion Cracking Experiences

The first reported indication of stress-corrosion failure came in early 1965 when a pressurized Ti-6Al-4V (solution-treated and aged) tank filled with liquid N_2O_4 ruptured at Bell Aerosystems Company.[80] Failure came after 40 hours' exposure at 105 F and a stress level of 90,000 psi. Microscopic examination of the tank disclosed a considerable number of cracks which had formed in all areas where the stress level was above 40,000 psi.

Following this discovery, NASA instituted a program to investigate the failure. A literature survey and a test program using tanks and test coupons was undertaken. Over 20 aerospace companies, government agencies, research firms, and universities cooperated in this study which was coordinated by The Bell Aerosystems Company for the National Aeronautics and Space Administration.

Some of the test results available to mid-March of 1966, are summarized in Tables 50 and 51. On the basis of these and other studies, the following conclusions can be made:

TABLE 48. CORROSION OF TITANIUM IN ORGANIC ACIDS[8]

Organic Acid	Type	Concentration, percent	Temperature, F	Corrosion, mpy
Acetic	Red.	5-99.5	Boiling	0 to 5
Citric	Red.-Complex.	50	Boiling	5 to 50
Formic (aerated)	Red.	10, 25, 50, 90	212	0 to 5
Formic (nonaerated)	Red.	25, 50, 90	Boiling	>50
Oxalic (aerated)	Red.-Complex.	0.5, 1.5, 10, 25	140	>50
Trichloroacetic	--	100	212	>50
Tartaric	Red.-Complex.	10-50	212	0 to 5
Stearic	--	100	356	0 to 5

TABLE 49. CORROSION OF TITANIUM ALLOYS IN FORMIC AND OXALIC ACID[28]

	Corrosion, mpy					
	95 F				190 F	
	Air Agitation		N_2 Agitation		No Agitation	
Alloy	25% Formic	5% Oxalic	25% Formic	5% Oxalic	25% Formic	5% Oxalic
Ti (75 BHN)(a)	R(b)	--	R	--	R	--
Ti (120 BHN)	R	38	R	52	R	1160
Ti 180 BHN)	R	21	R	33	R	700
Ti (200 BHN)	R	14	R	33	R	800
Ti-8Mn (annealed)	R	48	5	83	R	590
Ti-6Al-4V (annealed)	R	42	5	43	164	1580
Ti-6Al-4V (aged)	R	26	5	62	164	980
Ti-5Al-2.5Sn (annealed)	R	57	R	43	R	1880
Ti-8Al-2Cb-1Ta (annealed)	R	54	R	62	R	1420
Ti-2.5Al-16V (solution treated)	R	24	R	20	50	560
Ti-2.5Al-16V (aged)	R	23	R	21	50	990
Ti-1Al-8V-5Fe (annealed)	R	22	R	19	R	580
Ti-1Al-8V-5Fe (aged)	R	34	R	40	R	1040
Ti-3Al-2.5V (annealed)	R	23	R	25	R	1030

(a) BHN = Brinell Hardness Number.
(b) R = complete resistance.

TABLE 50. TESTS IN TANKS PRESSURIZED TO 250 PSIG, EQUIVALENT WALL STRESS OF 90,000 PSI(80)

Tanks	Propellant	Temperature, F	Time to Failure
(1) Ti-6Al-4V	Red[a] N_2O_4	85	200 hours
(2) Ti-6Al-4V	Red[a] N_2O_4	90 ± 88	51 to 192 hours
(3) Ti-6Al-4V	Red[a] N_2O_4	105	14 to 127 hours
(4) Ti-6Al-4V	Red[a] N_2O_4	160	6 to 12 hours
(5) Ti-6Al-4V + Teflon bladder	Red[a] N_2O_4	105	23 days
(6) Ti-6Al-4V (shot peened)	Red[a] N_2O_4	105	None after 30 days
(7) Ti-6Al-4V	Green[b] N_2O_4 + 1% NO	160	None after 30 days
(8) Ti-6Al-4V	Green[b] N_2O_4 + 0.3% NO + 0.8% Cl	--	None after 30 days

(a) "Red" N_2O_4 is conventionally prepared by bubbling oxygen through "green" N_2O_4. See Table 52 for specifications.
(b) "Green" N_2O_4 contains some NO. The composition of currently approved MSC-PPD-2 grade is given in Table 52.

TABLE 51. TESTS OF SPECIMENS(80)

Specimen[a]	Propellant	Temperature, F	Time to Failure
(1) Stressed	Red N_2O_4	165	90 hours or less
(2) Stressed	N_2O_4 + NO (0.1 to 1.7%)	165	No failure in 120 hours
(3) Stressed	N_2O_4 + H_2O (0.2 to 1.1%)	165	No failure in 120 hours
(4) Stressed	N_2O_4 + FNA (25% H_2O)	165	No failure in 120 hours

(a) Stress varied from 90 ksi to 140 ksi.

TABLE 52. COMPOSITION OF N_2O_4[a](80)

Element	Content, wt% Requirements of MIL-P-26539 A.	Requirements of NASA MSC-PPD-2
N_2O_4	99.5 minimum	99.5 minimum
H_2O (as HNO_3)	0.1 maximum	0.1 maximum
Cl (as NOCl)	0.08 maximum	0.08 maximum
NO	--	0.6 ± 0.20
Particulate matter	10 mg/c maximum	10 mg/c maximum

(a) In this work, the MIL-P-26539A grade has been called "red" and/or "white" while the MSC-PPD-2 grade "green". These designations arise from the color differences in various grades of N_2O_4 at 0 C. Thus, at 0 C, N_2O_4 of the MSC-PPD-2 grade is bluish-yellow or green while N_2O_4 containing no measureble NO content is yellowish or straw colored, i.e., "red" or "white" in comparison to the MSC-PPD-2 grade. At room temperature, all grades of N_2O_4 (including the MIL-P-26539A and MSC-PPD-2) are reddish-brown in color.

(1) Stress-corrosion cracking will usually occur in N_2O_4 when no significant or measurable amounts of NO are present and the system is exposed to moderately high stresses at temperatures in the range of 85 F to 165 F.

(2) Stress-corrosion cracking does not occur in N_2O_4 when the N_2O_4 contains an excess of NO.

(3) NO and O_2 are mutually incompatible, i.e., both cannot exist at the same time in N_2O_4. The following reaction is believed to occur:

$$2NO + O_2 \longrightarrow 2NO_2.$$

(4) The commercial and military specifications to which N_2O_4 is processed do not control either its O_2 or NO content. As a result of this work, NASA has developed a specification for N_2O_4 which controls the NO content (see Table 52).

(5) Stress-corrosion cracking in "red" N_2O_4 shows a time-temperature dependence as indicated in Table 50.

(6) A Teflon bladder is used in some of these tanks to contain the N_2O_4. The Teflon acts as a barrier but is permeable, in time, to N_2O_4. On occasion, tanks containing Teflon bladders filled with red N_2O_4 have failed after extended periods of time (see Test 5 in Table 50), and these have shown the same type of failure as where no bladder was used.

(7) Shot peening the inside surface of a tank so that there is no tensile stress on the inside diameter surface of the tank shell when in N_2O_4 service reduces the probability of stress-corrosion cracking.

(8) All tests to date have shown complete inhibition of stress-corrosion cracking of titanium in "green" N_2O_4 (see Table 52).

(9) Chloride addition as NOCl to "green" N_2O_4 up to the specification limit of 0.08 percent apparently does not initiate stress-corrosion cracking (see Test 8, Table 50).

(10) Further work has indicated that additions of sufficient water to red N_2O_4 will eliminate the stress-corrosion cracking of titanium. (This, in effect, adds NO and eliminates free oxygen since water forms nitric acid and NO in N_2O_4.)

Other work has shown that the primary cause of cracking is not related in any way to any titanium-processing operation. All normally accepted cleaning, heat treating, aging, welding, descaling, and handling techniques used for titanium have been checked. The stress-corrosion cracking susceptibility was not affected by any variation in these processes.

The crack propagation behavior of titanium in red N_2O_4 as compared with that for other environments was investigated in studies at Battelle for DMIC.[81] These tests were performed using a prefatigue-cracked specimen loaded dynamically under 3-point loading in an autoclave with a technique similar to that used in seawater tests as discussed by Brown.[82] Briefly, the specimens are step-loaded to a higher stress level every 4 to 8 minutes until failure occurs. The stress level is measured by the stress-intensity factor, K, in ksi $\sqrt{\text{inch}}$, assuming conditions of plane strain.

In air, step-loading resulted in failure at 70 ksi $\sqrt{\text{inch}}$. Similar results were found using the same techniques with red N_2O_4. However, when a specimen was step-loaded to just below the air value, and held for several days in red N_2O_4, stress cracks formed throughout the specimen and failure of the specimen occurred after 12 days at 127 F. During the experiment, relaxation of the stress was noted, indicating slow propagation of a crack, and the stress level had to be adjusted throughout the exposure period.

These results show that the rate of propagation of stress cracks is quite slow in N_2O_4 as compared with seawater. Time of exposure to the environment is, therefore, a much greater factor than it is in salt water, for example, where stress-corrosion failure can occur in a few minutes for some titanium alloys. Thus, the experimental procedure must be modified to evaluate stress-corrosion cracking in red N_2O_4 by the precracked specimen method.

In other short-term studies using precracked specimens, additions of 0.5 percent water (forming nitric acid and NO) and 0.25 percent concentrated hydrochloric acid (adding chlorides and water) were made to N_2O_4. The results again were similar to those in air.

Although the mechanism of stress-corrosion cracking of titanium in N_2O_4 is not fully understood, it is apparent that oxygen activity plays an important role, and that additions of NO inhibit the attack. It has been suggested that stress-corrosion cracking occurs on the titanium surface at coarse slip lines where the oxide film is not protective, or is easily ruptured, such as by local creep. This would account for the network of cracks associated with the failures. The NO addition could prevent this attack by removing the active oxygen and/or absorbing on the surface as a protective film. Chlorides have been suggested as a possible cause, since they are often associated with cracking. However, no proof of their contribution to the mechanism of cracking has been found. Work is continuing in these areas.

Further work is also indicated in the determination of what other alloys of titanium are susceptible, and on the character of the metal surface before and after exposure to N_2O_4.

Thermodynamic Considerations*

In an effort to explain the observed stress-corrosion-cracking failures, a limited study was undertaken by DMIC to collect and examine thermochemical data concerning the possible reactions that might be expected to occur between the Ti-6Al-4V alloy and the available grades of N_2O_4.

* This section of this memorandum was prepared by Dr. J. J. Ward, Fellow in the Materials Thermodynamics Division, Battelle Memorial Institute.

In brief, this study entailed the collection and/or estimation of the standard heat of formation and standard free energy of formation for 37 compounds representing possible reactants or reaction products. These were then used to calculate the standard heat of reaction, ΔH^o_R, and standard free energy of reaction, ΔF^o_R, that could possibly cause failure of titanium in N_2O_4 at both 77 and 260 F. Fifty-three reactions were postulated in which elemental titanium, aluminum, and vanadium were reacted with N_2O_4, NO, NO_2, NOCl, and/or mixtures of N_2O_4 with these impurities. Also, 25 reactions were postulated in which TiO, TiO_2, and TiN were reacted with N_2O_4 and these same impurities. All of these basic data and the reactions considered are given in Appendix A.

One obvious intent of this study was to determine what compounds of titanium could form that might be protective. Unfortunately, the results were almost completely negative. Thus, the thermodynamic indications were that virtually all of the 78 postulated reactions could occur and none of these offered any clues to support the experimental observations as to why an excess of NO suppresses the stress-corrosion reaction or why an excess of oxygen promotes this reaction.

Further, in all of these 78 reactions, the thermodynamics are relatively unchanged over the temperature range of 77 to 260 F. As pointed out earlier, however, a strong temperature dependence has been observed in the stress-corrosion behavior of the Ti-6Al-4V alloy in red N_2O_4 between 85 and 165 F. These differences between thermochemical prediction and experimental observation strongly suggest, therefore, that a reaction rate or mechanism is the cause of this reaction rather than a change in the thermodynamics of reaction over the temperature range of interest.

No thermodynamic data could be found for possible ions in nitrogen tetroxide as a solvent. The thermochemical data for aqueous solutions do not apply to ionic reactions in N_2O_4 (l), of course. The dielectric constants of N_2O_4 (l), compared with liquid benzene, NH_3 and H_2O as shown in Table 53 indicate that ionic reactions in N_2O_4 (l) are unlikely. This observation minimizes ionic reactions or electrochemical action as a cause for tank failure by stress-corrosion cracking.

TABLE 53. DIELECTRIC CONSTANTS OF LIQUID N_2O_4 AND SEVERAL OTHER LIQUIDS[83]

Compound	Dielectric Constant ϵ (ϵ vacuum^{-1})	Temperature, C
N_2O_4(l)	2.5	15
Benzene(l)	2.284	25
Ammonia(l)	16.9	25
Water(l)	78.54	25

CORROSION IN LIQUID METALS

Liquid metals are encountered in three types of service: alloying and melting operations, chemical operations in which one or more reactants are liquid metals, and as a high-temperature, heat-transfer medium. This latter use is becoming more important as a result of the increasing interest in high-temperature atomic-reactor power systems. Several important physical properties of liquid metals which are of potential use as reactor coolants are illustrated in Figure 5.

Titanium is of interest as a construction material for liquid-metal systems. However, because of the loss of mechanical properties and poor corrosion resistance to a number of the liquid metals, the present use of titanium and its alloys in such environments is restricted.

The following paragraphs briefly describe the behavior of titanium in some of these media.

Bismuth - Lead Alloy (55.5Bi-44.5Pb)

In 500 hour tests at 1200 F, a Ti-4Cr alloy showed excellent resistance to the 55.5Bi-44.5Pb eutectic alloy.[85] Under the same conditions of exposure, alloys of Ti-1Si and Ti-5Cu showed moderate and poor resistance, respectively.

Cadmium

In 1956 and 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.[39] 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.

Cesium

Although general corrosion is not reported, liquid cesium appears to degrade the physical properties of titanium. For example, at 750 F, the weight changes for Ti-6Al-4V specimens in either a titanium or type 347 stainless steel container were from +0.2 to -0.8 mg/sq dec/day for both vapor and liquid exposure.[86] This is a penetration rate of less than 0.2 mil per year. However, after exposure to liquid cesium, the ductility of unalloyed titanium, Ti-30V, Ti-6Al-4V, and Ti-13V-11Cr-3Al, as measured by bending, is reduced (see Table 54).

The tensile properties of titanium are also decreased by exposure to cesium at 392 F as shown in Table 55.[87] Titanium is apparently attacked more in the vapor than in the liquid. The reduction in tensile properties is less at very slow pull rates.

Tension-tension fatigue tests in liquid cesium at 86 to 95 F showed essentially no adverse effect. Specimens studied included sheet specimens of unalloyed titanium, Ti-6Al-4V, and Ti-13V-11Cr-3Al, as well as 302 stainless steel, Kovar, NiSpan-C, 1040 steel and molybdenum.[87]

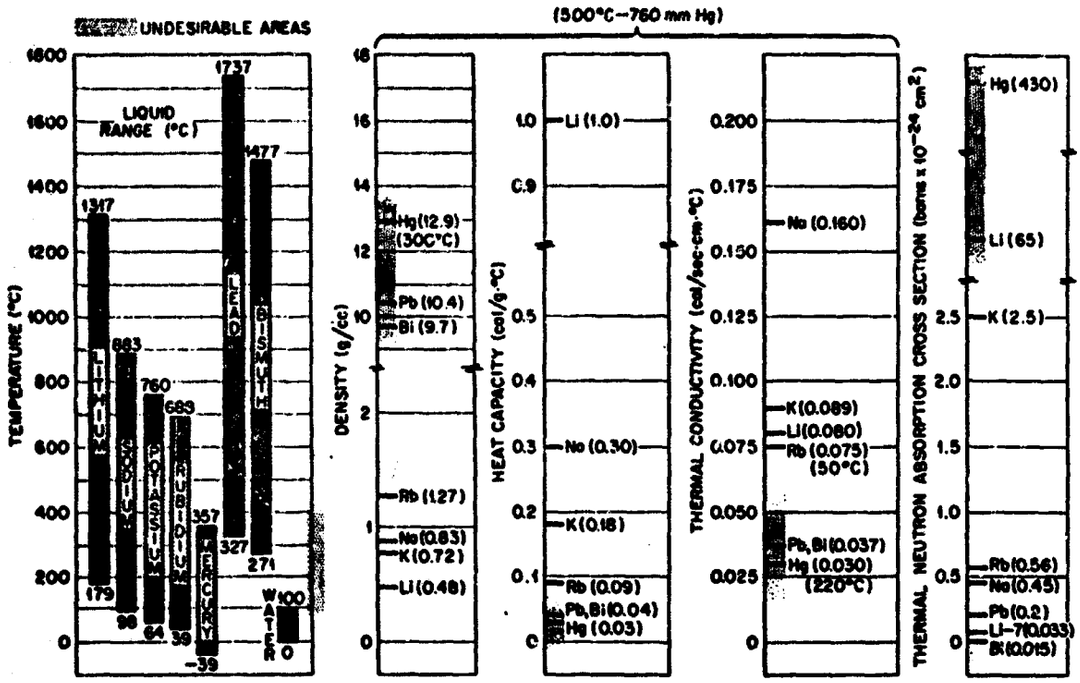

FIGURE 5. SOME IMPORTANT PHYSICAL PROPERTIES OF POTENTIAL REACTOR COOLANTS

TABLE 54. BEND DUCTILITY OF TITANIUM AFTER EXPOSURE TO LIQUID AND VAPOR CESIUM(87)

Alloy	Treatment	Bending, 86 F Dry	Bending, 86 F Cs	Stress to Yield 1000 Hr at 86 F Cs	180° Bending After 1000 Hr Exposure 86 F	90° Bending After 1000 Hr 1200 F Cs Vapor
Ti	As-received	Okay	Fractures	Okay	Large cracks	Fractured
Ti-30V	As-forged	Small cracks	Fractures	Okay	Fractures	Large cracks
Ti-6Al-4V	Mill-anneal	Okay	Fractures	Okay	Small cracks	Fractures
Ti-13V-11Cr-3Al	Mill-anneal	Small edge cracks	Many small cracks	Okay	Small cracks	Fractures

TABLE 55. TENSILE STRENGTH OF TITANIUM ALLOYS IN LIQUID AND VAPOR CESIUM AT 392 F AT VARIOUS PULL RATES(87)

Alloy	Environment	Pull Rate, in./min(a)	Ultimate Tensile Strength, ksi	Yield Strength, ksi	Elongation, percent
Ti	Dry	0.5	74.0	63.0	20.0
Ti	Cs	0.5	70.0	60.0	21.8
Ti	Cs	0.5	71.0	59.6	20.4
Ti	Cs vapor	0.5	50.0	44.0	13.1
Ti	Cs vapor	0.5	48.0	37.0	10.8
Ti	Cs	0.1	68.8	55.0	30.3
Ti	Cs	0.01	68.0	53.0	28.8
Ti	Cs	0.01	59.0	53.0	29.5
Ti-6Al-4V	Dry	0.5	161.0	152.0	12.4
Ti-6Al-4V	Cs	0.5	151.0	142.0	11.2
Ti-6Al-4V	Cs	0.5	152.0	143.0	11.8
Ti-6Al-4V	Cs vapor	0.5	126.0	112.0	7.5
Ti-6Al-4V	Cs vapor	0.5	125.0	110.0	7.7
Ti-6Al-4V	Cs	0.1	148.3	138.0	10.2
Ti-6Al-4V	Cs	0.01	157.0	141.0	12.9
Ti-6Al-4V	Cs	0.01	147.0	135.0	12.8

(a) Specimens 1/8-inch diameter, 1-1/4-inch gage length.

Gallium

Titanium is disintegrated by gallium[88,89] at 840 F, but is reported[90] to have good resistance at 750 F.

Lead

Titanium[1,91] has poor resistance to lead at 1500 and 1830 F.

Lithium

Titanium, molybdenum, tantalum, zirconium, vanadium, and beryllium were found to be quite resistant to attack by lithium.[84,92] (In early work, some of the above were thought to have poor resistance because of dissimilar metal transfer from iron capsules.) Titanium shows no attack at 1500 F (see Table 56).[92] At 1830 F only fair resistance is reported for titanium.[93] Figure 6 compares the static and dynamic corrosion resistance of several materials. However, the texts of references 84 and 92 indicate that titanium was not tested in the flowing systems. Pure iron, ferritic chromium stainless steel, columbium, tantalum, and molybdenum appear to have superior resistance to lithium.[93]

The impurity levels in lithium may also affect the rate of attack of titanium. For instance, the solubility of titanium increases with both nitrogen concentration and temperature as shown in Figure 7.[94] Although oxygen was not found to alter the corrosion resistance of titanium to lithium, transfer between lithium and titanium does occur. The equilibrium concentration in titanium appears to be between 700 and 900 ppm O_2 after 100 hours at 1500 F.[94]

Magnesium

Early work[95] has indicated that titanium has good resistance to magnesium up to 1380 F and limited resistance at 1560 F. However, the Ti-Mg phase diagram indicates appreciable solubility in liquid magnesium.

Mercury

Titanium, in itself, is not very resistant to mercury, except at low temperatures.[96,97](a) Because of its light weight and high strength,

(a) Some room-temperature corrosion data for titanium in mercury and some mercury alloys are given in the Low-Temperature Alloys section of this memorandum.

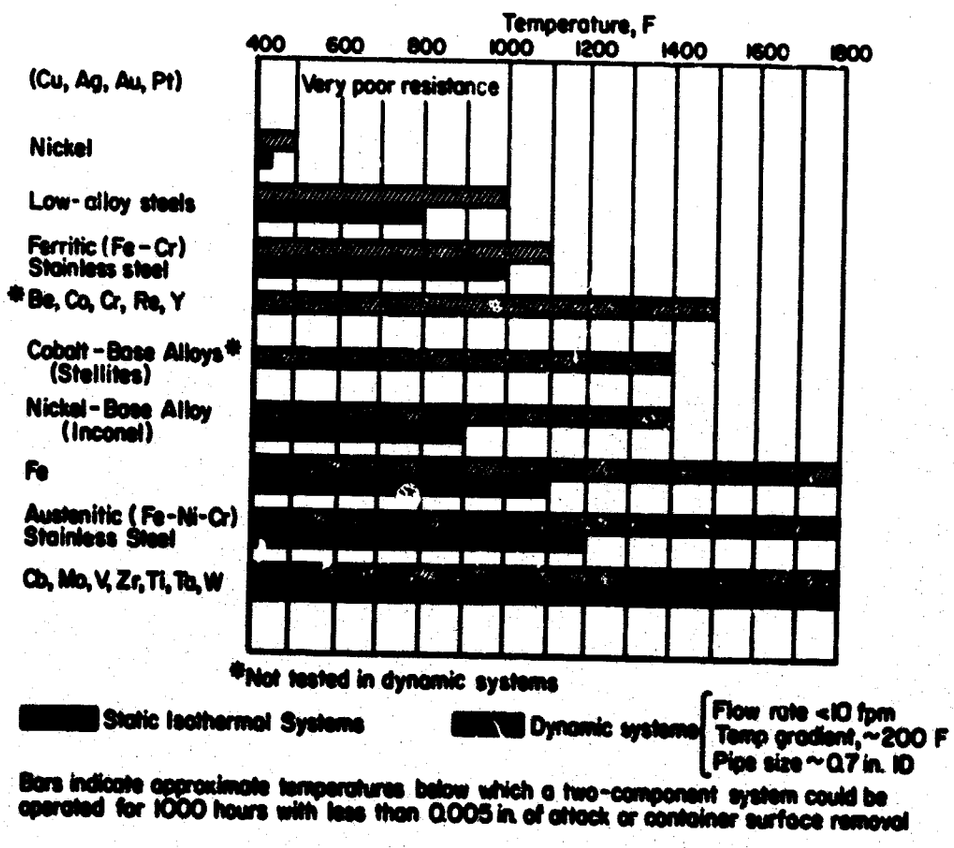

FIGURE 6. CORROSION RESISTANCE OF VARIOUS METALS AND ALLOYS IN MOLTEN LITHIUM[92]

TABLE 56. RESULTS OF LITHIUM CORROSION TESTS ON METALS IN TWO-COMPONENT STATIC TEST SYSTEMS[92]

Metal	Temperature F	Temperature C	Time, hours	Surface Area / Volume of Lithium, in.^{2}/in.^{3}	Weight Change, mg/in.^{2}	Metallographic Observations
Beryllium	1500	816	100	10	+1.7	2 mils of intergranular attack
Beryllium	1832	1000	100	10	+1.6	3 mils of intergranular attack
Copper[a]	1500	816	100	13	--	Portions of 35-mil tube wall completely dissolved
Iron[a]	1500	816	100	13	0	No attack
Iron	1500	816	400	7	-2.0	Up to 20 mils of very faint intergranular penetration
Iron	1832	1000	400	7	-1.9	No attack
Molybdenum	1500	816	100	13	0	No attack
Nickel[a]	1500	816	100	13	--	Portions of 35-mil tube wall completely dissolved
Tantalum	1500	816	100	13	+7.6	No attack
Titanium[a]	1500	816	100	13	+2.5	No attack
Vanadium	1500	816	100	13	+8.4	No attack
Zirconium	1500	816	100	13	0	No attack

(a) Duplicate tests.

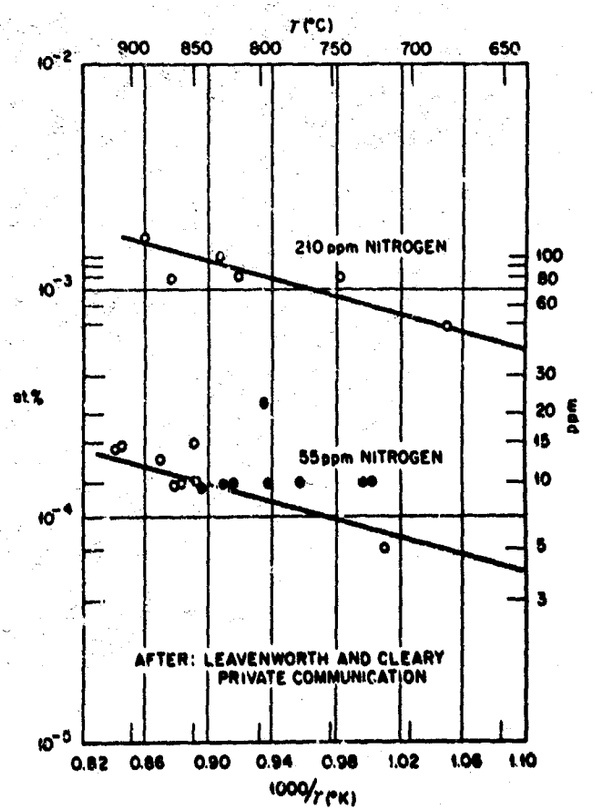

FIGURE 7. SOLUBILITY OF TITANIUM IN LITHIUM[94]

considerable research has been done on improving the corrosion resistance of titanium to mercury, especially at elevated temperatures.

Commercially available titanium and its alloys are corroded at about 1 mil per month in mercury at 700 F.[96] A thin adherent black film was present on most surfaces. Little attack occurred in the vapor. Based on static-test data, it seems unlikely that any of the present titanium alloys would be satisfactory by themselves.[96] Tables 57 and 58 give corrosion data for various alloys in mercury at temperatures of 700 through 1000 F.

Possible Stress-Corrosion Cracking

A 1962 reference,[96] 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.[98] Wetting of unstressed titanium by mercury requires a temperature of 750 F in vacuum, while reexposure to air causes dewetting.[98] 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.

Surface Protection

Corrosion of titanium by mercury can be reduced by protection of the titanium surface. Nitrided titanium alloys (see Table 59),[97] Ti-2.5Al-16V and Ti-7Al-12Zr suffered no attack after 14 days in mercury at 1000 F or 41 days at 850 F.[96,97] At 1000 F some selective attack

TABLE 57. RESULTS OF MERCURY CORROSION TESTS ON TITANIUM AND TITANIUM ALLOYS AT 700 F (STATIC SYSTEM)[97]

Material	Test Environment	Test Period, hours	Weight Change,[a] mg/cm^2	Remarks
Commercially Pure Titanium	Liquid Hg	168	-26.22	Slightly pitted
		720	-79.7	Pitting attack to depth of 2 mils
	Hg vapor	720	Nil	No attack
Crystal Bar Titanium	Liquid Hg	336	-14.2	Uniformly corroded
Ti-4Al-4Mn (alpha-beta type)	Hg vapor	720	+ 0.02	No attack
	Liquid Hg	720	- 7.22	Scattered attack all over
Ti-8Mn (alpha-beta type)	Hg vapor	720	+ 0.04	One crack
	Liquid Hg	720	- 9.48	Scattered attack all over
Ti-7Al-4Mn (alpha-beta type)	Hg vapor	720	Nil	No attack
	Liquid Hg	720	-16.12	Attack in several scattered areas
Ti-3Al-2.5V (alpha-beta type)	Hg vapor	720	+ 0.05	No attack
	Liquid Hg	720	+10.06	Uniformly corroded
Ti-2.5Al-16V (alpha-beta type)	Liquid Hg	336	- 0.45	Slightly cracked
Ti-6Al-4V (alpha-beta type)	Hg vapor	720	Nil	One crack
	Liquid Hg	720	- 2.94	One crack; attack in several scattered areas
Ti-3Al-5Cr (alpha-beta type)	Hg vapor	336	Nil	No attack
	Liquid Hg	336	- 0.95	Very lightly attacked
Ti-5Al-2.5Sn (alpha type)	Hg vapor	720	Nil	One crack
	Liquid Hg	720	- 5.54	One crack; shallow pits
Ti-8Al-2Cb-1Ta (alpha type)	Hg vapor	720	+ 0.03	Four cracks
	Liquid Hg	720	- 9.41	Uniformly corroded
Ti-8Al-8Zr-1(Cb + Ta) (alpha type)	Hg vapor	336	+ 0.01	One small crack
	Liquid Hg	336	- 4.48	Many cracks
Ti-7Al-12Zr (alpha type)	Hg vapor	336	- 0.01	No attack
	Liquid Hg	336	- 3.83	One long crack; solution type attack
Ti-5Al-5Sn-5Zr (alpha type)	Liquid Hg	336	+ 1.11	Cracked and pitted
Ti-8Al-1Mo-1V (alpha type)	Liquid Hg	336	+ 0.57	Slightly cracked
Ti-13V-11Cr-3Al (beta type)	Hg vapor	720	Nil	Severely cracked
	Liquid Hg	720	- 8.10	Severely cracked

(a) "+" refers to weight gain and "-" refers to weight loss.

TABLE 58. CORROSION TESTS RESULTS ON TITANIUM AND TITANIUM ALLOYS IN LIQUID MERCURY AT 850 AND 1000 F (STATIC SYSTEM)[97]

Material	Test Period, hours	Weight Loss, mg/cm^2 850 F	Weight Loss, mg/cm^2 1000 F	Remarks
Commercially Pure Titanium	720	-26.48	--	Uneven attack
	336	--	-49.14	Uniformly corroded
Ti-2.5Al-16V (alpha-beta type)	720	- 5.57	--	Slightly pitted
	336	--	-21.47	Thin layer of corrosion product; uniformly attacked
Ti-3Al-5Cr (alpha-beta type)	720	-38.20	--	Uniformly corroded
	336	--	-53.90	Black corrosion product, irregularly distributed
Ti-7Al-12Zr (alpha type)	720	- 6.50	--	Shallow pits
	336	--	-77.56	Uneven, severely corroded
Ti-8Mn (alpha-beta type)	720	-40.50	--	Uniformly attacked
	336	--	-61.35	Severe, uneven surface attack

TABLE 59. WEIGHT CHANGE, mg/cm^2, OF TITANIUM AND TITANIUM ALLOYS AFTER 14 DAYS' EXPOSURE IN MERCURY AT 538 C (STATIC SYSTEM)(97)

Materials	As-Polished (Liquid Only)	Nitrided Liquid	Nitrided Vapor
Commercially pure titanium	-49.14	+0.78	-0.51 (30 days)
Commercially pure titanium	--	+0.12(a)	--
Ti-2.5Al-16V	-21.47	+0.11	+1.12
Ti-3Al-5Cr	-55.90	+0.08	+0.64
Ti-7Al-12Zr	-77.56	+0.07	+2.82
Ti-8Mn	-61.35	+0.13	+0.40

(a) Heat treated at 800 C for 4 hours under vacuum.

occurred on corners.(96) The nitrides on Ti-7Al-12Zr and Ti-3Al-5Cr are susceptible to attack in the vapor phase. The nitrided layer on unalloyed titanium cracks although little weight loss occurs. The manganese in Ti-8Mn may obstruct the N_2 diffusion into the metal. However, a very adherent film is formed.

An attempt to carburize titanium alloys for resistance to mercury was unsuccesful. The surface became brittle and cracked, possibly because of hydrogen absorption.(97) A sulfuric anodized film of thickness 5 to 11 microinches protected titanium at 700 F, but dissolved at 850 F.(97)

Metal Additives

The addition of metal additives to mercury tends to decrease its attack of titanium. Effective additives are zirconium, nickel, aluminum, copper, iron, magnesium, or cadmium.(97,99,100,101,102) The addition of bismuth or zinc increases the attack on titanium. Beryllium has no effect.(97) At 700 F, additions to mercury reduce the weight loss of commercially pure titanium from 26.2 mg/cm^2 (7 days) to 1.43 for magnesium, 1.37 for iron, 1.09 for copper, and 0.56 for zirconium, all after 14 days.(101) The effect of metal additives on the solubility of titanium in mercury at 700 F is shown in Table 60.

TABLE 60. SOLUBILITY OF TITANIUM AND METALLIC ADDITIVES IN LIQUID MERCURY AT 700 F(97)

Materials Tested	Equilibrium Solubility of Metallic Elements in Liquid Hg, ppm: Ti	Cu	Fe	Zr	Be
Ti	13.20	--	--	--	--
Ti + Cu	6.70	214	--	--	--
Ti + Fe	7.22	--	0.56	--	--
Ti + Zr	8.50	--	--	241	--
Ti + Be	13.50	--	--	--	0.06

As shown in Table 61, separate additions of zirconium, aluminum, and nickel reduce the attack of mercury on titanium at 1000 F. However, binary combinations of these additives in mercury tend to accelerate the attack of titanium at 1000 F.

In thermal loops, single metal additives to mercury proved less effective than was indicated in the above work. Thus, in a thermal loop at 850 F, with or without added zirconium, the hot leg specimens of titanium were dissolved.(102) Also, in a loop with a nickel additive, mass transfer of nickel to the titanium hot leg sample occurred.(103)

Based on the above data, the applicability of titanium for mercury service is limited. Additional data should be obtained before any such use is planned.

Potassium, Sodium, and NaK Alloys

Titanium appears to offer good resistance to sodium, potassium, and NaK alloys up to 1000 to 1100 F. Above 1100 F, the corrosion rate is significant and titanium is limited to short-time use. Both nickel and 18-8 stainless steels appear to have better resistance in these media than titanium.(93)

The effect of cavitation on the corrosion resistance of unalloyed titanium (Grade Ti 100A) in sodium up to 1000 F is a function of time and temperature.(104) Tests were performed using a magnetostrictive oscillator in sodium containing total O_2, N_2, and H_2O of <5 ppm. The cavitation damage was found to occur in four steps, listed below, and is illustrated in Figure 8.

(1) Incubation
(2) Accumulation
(3) Attenuation
(4) Steady State.

The steady-state cavitation damage was then shown to vary with temperature as in Figure 9.

In addition, amplitude of the oscillation was found to affect the rate of weight loss, as shown in Figure 10. The steady-state weight loss varies as the square of the displacement amplitude, as also shown in water systems. The intensity of cavitation damage in sodium at 400 F is about one and one-half times that in water at 80 F for a given amplitude and frequency.

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.(105) 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

TABLE 61. INTERACTION OF CRYSTAL BAR TITANIUM AND ADDITIVES EXPOSED TO LIQUID MERCURY AT 1000 F (STATIC SYSTEM)[102]

Exposure to Liquid Mercury Plus	Weight Change in 14 Days,[a] mg/sq cm	Spectrochemical Analysis of Exposed Surfaces[b]				
		Hg	Ni	Zr	Mg	Al
No additives	-16.51	W	--	T	--	--
	-17.60	W	--	T	--	--
	-18.69	W	--	T	--	--
Ni (750 ppm)	+ 4.04	M	M	--	--	--
	+ 3.92	M	M	--	--	--
Ni (750 ppm) + Mg (50 ppm)	-34.10	W	T	--	--	--
	-31.20	W	T	--	--	--
Ni (750 ppm) + Al (50 ppm)	-28.56	M	W-M	--	--	W-M
	-29.87	M	W-M	--	--	W-M
Al (750 ppm)	+ 0.26	M	--	--	--	S-VS
	+ 0.32	M	--	--	--	S-VS
Ni (750 ppm)	- 0.15	M	--	M	--	--
	- 0.94	M	--	M	--	--
	- 0.92	M	--	M	--	--
Zr (750 ppm) + Al (50 ppm)	- 0.89	S-VS	--	--	--	VS
	- 1.56	S-VS	--	--	--	VS
Zr (750 ppm) + Mg (50 ppm)	- 2.08	M	--	S	--	--
	- 1.07	M	--	S	--	--

(a) "+" refers to weight again, "-" refers to weight loss.
(b) VS - very strong, above 10 percent; S - strong, 10 to 1 percent; M - moderate, 1 to 0.1 percent; W - weak, 0.1 to 0.01 percent; T - trace, 0.01 to 0.001 percent.

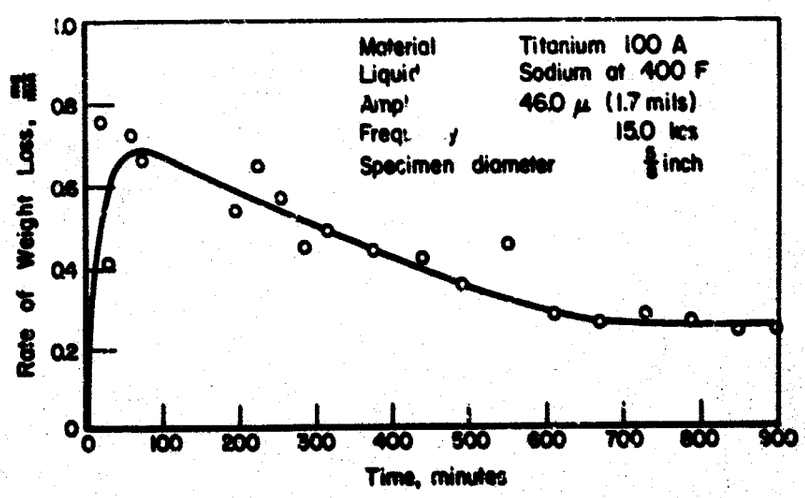

FIGURE 8. CAVITATION DAMAGE, EFFECT OF TIME ON RATE OF WEIGHT LOSS OF 100 A TITANIUM[104]

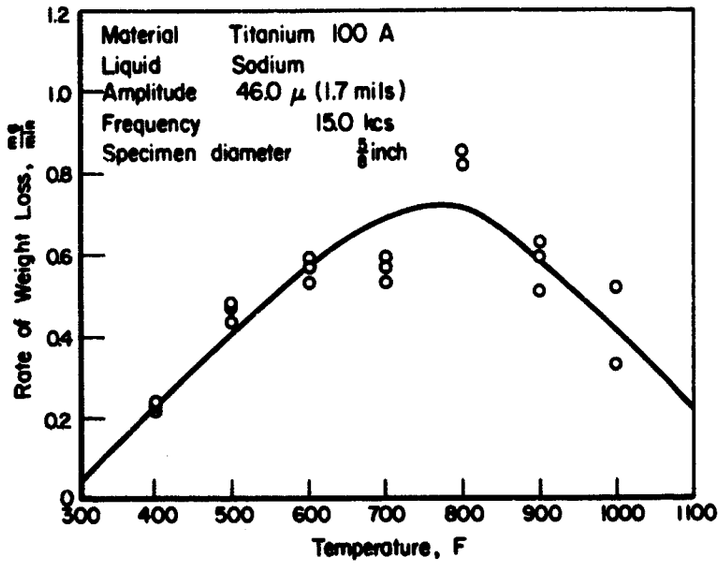

FIGURE 9. STEADY-STATE CAVITATION DAMAGE, EFFECT OF LIQUID-METAL TEMPERATURE ON RATE OF WEIGHT LOSS[104]

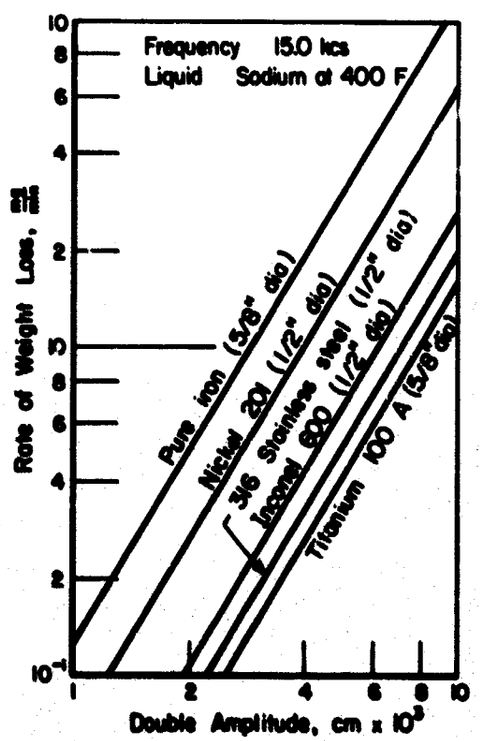

FIGURE 10. EFFECT OF DISPLACEMENT AMPLITUDE ON THE RATE OF WEIGHT LOSS[104]

hours. 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 hours.

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.(106) 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 62. 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 on 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 antifretting 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.

TABLE 62. RESULTS OF STRESS-CORROSION STUDIES OF TITANIUM ALLOYS WITH SILVER AND SILVER CHLORIDE(106)

Temperature, F	Stress, ksi	Coating	Failure Time, hours
		Ti-7Al-4Mo	
800	100	Bare	40-396
800	100	NaCl	1.4 to 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 (vacuum deposit)	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, 669
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 to 153 ksi, El 10-to 11 percent.
(e) Hydraulic oil.

Tin

Titanium showed excellent resistance,(1) to tin at 930 F.

Low-Temperature Alloys

In a survey of the corrosion properties of metals exposed to liquid metals at room temperature, none of the liquid metals tested were found to be detrimental to unalloyed titanium A-70.(107) Exposure was carried out at 77 to 91 F with a relative humidity of 80 percent. Prior to exposure to the liquid metal, an ethanol-HCl etchant and several fluoride etchants were applied to the titanium:

(1) HgF_2 + 2M HF
(2) 1M HF
(3) NaF + 2M H_2SO_4
(4) Ethanol - HF
(5) 2M HCl - 0.2M NaF.

No evidence of oxidation, cracking, or loss of coherence was observed for the liquid metals shown in Table 63.(107)

TABLE 63. LIQUID METALS EXPOSED TO Ti A70 AT ROOM TEMPERATURE WITHOUT OXIDATION CRACKING OR LOSS OF COHERENCE(107)

Hg	Ga	98Hg-2Ga saturated In
Hg saturated Ag	Ga saturated Ag	98Hg 2Ga saturated Tl
Hg saturated As	Ga saturated Cu	
Hg saturated Au	Ga saturated Ni	95Hg-5Ga saturated In
Hg saturated Ba	Ga saturated Pb	95Hg-5Ga saturated Tl
Hg saturated Cu	Ga saturated Tl	
Hg saturated In		95Hg-5Tl saturated In
Hg saturated Mg	82Ga-18In	
Hg saturated Mn	80Ga-20In	73Hg-17In-10Tl
Hg saturated Pd	65Ga-35In	51Hg-41In-8Tl
Hg saturated Pt		
Hg saturated Rh	95Ga-5Sn	80Hg-18Tl-2Pb
Hg saturated Ru	92Ga-8Sn	
		70Ga-18In-12Sn
95Hg-5Ga	95Ga-5Zn	
90Hg-10Ga		82Ga-12Sn-6Zn
75Hg-25Ga	90Ga-10Cd	
70Hg-30Ga		
	98Hg-2Bi	
95Hg-5In		
90Hg-10In	98Hg-2Pb	
80Hg-20In		
70Hg-30In	98Hg-2Sn	
95Hg-5Tl	98Hg-2Zn	
90Hg-10Tl		
80Hg-20Tl	95Hg-5Cd	
70Hg-30Tl		

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APPENDIX A

THERMODYNAMIC CONSIDERATIONS FOR REACTIONS OF Ti-6Al-4V WITH NITROGEN TETROXIDE

J. J. Ward*

A limited study was undertaken by DMIC to collect and examine thermochemical data concerning the possible reactions that might be expected to occur between the Ti-6Al-4V alloy and the available grades of N_2O_4.

To this end, the standard heat of formation, ΔH^o_f, and standard free energy of formation, ΔG^o_f, of a number of compounds of interest were collected or estimated for temperatures from 0 to 400 K (-459 to 260 F). These are given in Table A-1. The compounds in this table were selected on the basis of liquid N_2O_4 and its nominal impurities (see Table 52) and the postulated reaction products of these with titanium, aluminum, and vanadium.

The values of ΔH^o_f of the compounds in Table A-1 were used to calculate the standard heat of reaction and standard free energy of reaction that could possibly cause failure of titanium in N_2O_4. Eighty-five reactions were postulated and grouped as follows:

(a) Changes of state or reactions between N_2O_4, NO, NO_2, O_2, and H_2O

(b) Reactions of elemental Ti, Al, and V with N_2O_4

(c) Reactions of elemental Ti, Al, and V with N_2O_4 impurities

(d) Reactions of TiO, TiO_2, and TiN with N_2O_4 and impurities in N_2O_4.

Five other reactions (Group E) were also postulated in considering the possibility of chloride removal from N_2O_4 through the use of silver additions. These 90 reactions and thermochemical data for them at 77 and 260 F are given in Table A-2.

The reactions shown in Table A-2 with a negative sign for ΔG^o_R can occur if the reactants and products are in their standard states.

The standard state for gases is taken at one atmosphere for the ideal gas. In the case of solids, the standard state is a crystalline bulk state. Liquids are considered at one atmosphere pressure. An example of solid-state reaction is 61, Table A-2, as:

$$Ti(c) + TiO_2(c) \rightleftharpoons 2TiO(c).$$

If $TiO_2(c)$ or TiO(c) are protective films, a free-energy value would be required for the change from a bulk state to a film as

$$2TiO(c) \rightleftharpoons 2TiO\ (film)$$

and

$$TiO_2(c) \rightleftharpoons TiO_2\ (film).$$

The free energy of the foregoing reactions was not taken into account because of a lack of data on surface effects. For similar reasons, the free energy of solutions of NO(g) in $N_2O_4(l)$ and other solution effects were not calculated.

The equilibrium constant, K_R, of reaction can be calculated from the values of ΔF^o_R by the equation:

$$\Delta G^o_R = -RT \ln K_R .$$

With the equilibrium constant, K_R, the equilibrium extent of reaction can be calculated under conditions of activity and concentration that are different from the standard state. The effect of pressure on a reaction can be evaluated from the relationship,

$$\frac{\partial \Delta G^o}{\partial P} = \Delta V .$$

In general, if the number of gaseous moles of reactant is greater than the number of gaseous moles of product, the extent of reaction is greater with an increase in pressure at equilibrium.

It should be emphasized that the value of the standard free energy of formation is only an indication of the possibility of a reaction. The ΔF^o_R value gives no information on reaction rate nor time requirement for the initiation of a reaction. The time dependency belongs to the study of reaction kinetics and mechanism.

Comments on the negative results suggested by the 78 postulated Groups B, C, and D reactions have previously been summarized in the body of this memorandum.

So far as the Group A reactions are concerned, Reactions 2 and 3 indicate that H_2O additions to N_2O_4 to form HNO_3 and NO (with or without NO_2) are not favored in the absence of oxygen. In the presence of oxygen (Reaction 5), HNO_3 formation from H_2O and N_2O_4 is favored. Completion of this reaction would also be promoted with increasing pressure. This suggests than any beneficial effects ascribed to H_2O additions may arise only where some free oxygen is present.

Reaction 6 supports the incompatibility of mixtures of oxygen and NO.

The Group E reactions were considered since there is some question as to whether or not the chloride might be contributing to the stress-corrosion problem. If this concern persists, then the use of a silver film or ion might be considered to remove the chloride as NOCl by precipitation to AgCl as shown in Reactions 87 and 89. This assumes that AgCl is as insoluble in N_2O_4 as it is in water, which is likely.

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TABLE A-1. THERMOCHEMICAL DATA[a] FOR COMPOUNDS OF INTEREST IN THE COMPATIBILITY STUDY OF NITROGEN TETROXIDE IN TITANIUM METAL

		Standard Heat of Formation, ΔH_f°, kcal/gmol, at Indicated Temperatures, Kelvin						Standard Free Energy of Formation, ΔG_f°, kcal/gmol, at Indicated Temperatures, Kelvin					
No.	Compound	0	100	200	298	300	400	0	100	200	298	300	400
1	TiO(c)	-123.186	-123.572	-123.844	-123.900	-123.900	-123.838	-123.186	-121.486	-119.200	-116.892	-116.848	-114.505
2	Ti_2O_3(c)	-360.923	-362.039	-362.782	-362.900	-362.898	-362.611	-360.923	-355.711	-348.978	-342.224	-342.096	-335.194
3	TiO_2(c)	-224.347	-225.012	-225.417	-225.500	-225.500	-225.391	-224.347	-220.919	-216.635	-212.283	-212.201	-207.780
4	TiN(c)	-79.625	-80.026	-80.367	-80.500	-80.501	-80.491	-79.625	-78.028	-75.897	-73.637	-73.595	-71.292
5	$TiCl_2$(c)	-	-	-	-123.500	-123.494	-123.184	-	-	-	-112.970	-112.904	-109.422
6	$TiCl_2$(g)	-72.193	-72.245	-72.275	-72.300	-72.301	-72.349	-72.193	-73.004	-73.749	-74.464	-74.478	-75.197
7	$TiCl_4$(c,ℓ)	-195.803(c)	-196.146(c)	-195.667(c)	-192.300(ℓ)	-192.277(ℓ)	-191.073(ℓ)	-195.803(c)	-189.122(c)	-182.259(c)	-176.319(ℓ)	-176.219(ℓ)	-171.051(ℓ)
8	*$Ti(NO_3)_2$(c)	-	-	-	-	-	-	-	-	-	-127.0	-	-
9	*$TiO(NO_3)_2$(c)	-	-	-	-	-	-	-	-	-	-190.0	-	-
10	$AlCl_3$(c)	-168.299	-166.978	-168.912	-168.580	-168.573	-168.160	-168.299	-162.784	-156.592	-150.616	-150.505	-144.543
11	Al_2O_3(c)	-397.494	-398.697	-399.838	-400.400	-400.406	-400.555	-397.494	-392.241	-385.329	-378.078	-377.940	-370.418
12	VO(c)	-	-	-	-98.000	-	-97.800	-	-	-	-91.400	-	-89.100
13	V_2O_3(c)	-	-	-	-296.000	-	-295.600	-	-	-	-276.970	-	-268.150
14	VCl_2(c)	-	-	-	(-117.000)	-	(-116.550)	-	-	-	(-105.900)	-	(-102.100)
15	VN	-	-	-	(-40.800)	-	(-40.750)	-	-	-	-34.550	-	-32.400
16	AlN	-	-	-	-76.000	-76.004	-76.149	-	-	-	-68.595	-68.549	-66.038
17	N_2O_4(g)	+4.473	+3.319	+2.563	+2.170	+2.165	+2.035	+4.473	+9.721	+16.446	+23.355	+23.486	+30.619
18	N_2O_4(ℓ)	(-4.488)	(-6.599)	(-5.789)	-4.676	-4.652	(-3.142)	(-4.488)	(+3.775)	(+13.863)	+23.282	+23.455	(+32.607)
19	N_2O_4(c)	-7.263	-8.601	-8.833	(-8.373)	(-8.358)	(-7.141)	-7.263	+2.174	+13.095	(+23.785)	(+23.984)	(+34.600)
20	NO(g)	+21.456	+21.256	+21.558	+21.580	+21.580	+21.590	+21.546	+21.256	+20.984	+20.697	+20.692	+20.394
21	N_2O(g)	+20.430	+20.084	+19.786	+19.610	+19.608	+19.530	+20.430	+21.573	+23.185	+24.896	+24.928	+26.716
22	NO_2(g)	+8.586	+8.326	+8.099	+7.910	+7.907	+7.770	+8.586	+9.545	+10.853	+12.247	+12.247	+13.751
23	NO_3(g)	+18.529	+17.912	+17.375	+17.000	+16.995	+16.815	+18.529	+20.985	+24.272	+27.745	+27.811	+31.449
24	N_2O_5(g)	-	-	+3.036	+2.700	+2.697	+2.710	-	-	+19.848	+28.186	+28.343	+36.898
25	HNO_3(ℓ)	-	-	-	-41.349	-	-	-	-	-	-19.030	-	
26	N_2O_3(g)	-	-	-	+19.800	+19.787	+19.691	-	-	-	+33.324	+33.408	+37.965
27	HNO_3(g)	-29.755	-30.749	-31.527	-32.100	-32.109	-32.472	-29.755	-26.696	-22.332	-17.690	-17.601	-12.704
28	NOCl(g)	-	-	-	+12.620	+12.619	+12.602	-	-	-	+16.049	+16.070	+17.224
29	NO_2Cl(g)	-	-	-	+6.310	+6.307	+6.185	-	-	-	+16.300	+16.361	+19.734
30	H_2O(ℓ)	-	-	-	-68.320	-	-	-	-	-	-56.720	-	-
31	H_2O(g)	-57.103	-57.433	-57.579	-57.798	-57.803	-58.042	-57.103	-56.559	-55.635	-54.636	-54.617	-53.519
32	HCl(g)	-22.019	-22.063	-22.029	-22.063	-22.064	-22.129	-22.019	-22.289	-22.535	-22.778	-22.782	-23.012
33	NH_3(g)	-9.362	-10.052	-10.508	-11.040	-11.050	-11.572	-9.362	-8.205	-6.195	-3.966	-3.923	-1.467
34	NH_4Cl(c)	-	-	-	-75.380	-75.380	-75.222	-	-	-	46.743	-48.578	-39.660
35	AgCl	-	-	-	-30.362	-	-	-	-	-	-26.224	-	-
36	$AgNO_3$	-	-	-	-29.430	-	-	-	-	-	-7.690	-	-
37	Ag_2O	-	-	-	-7.306	-	-	-	-	-	-2.586	-	-

* Estimated values.

(a) Numerical values carried beyond the significant place for computational consistency. The following references were used as sources for the data contained in this table:

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TABLE A-2. THERMOCHEMICAL DATA FOR POSTULATED REACTIONS OF INTEREST IN THE COMPATABILITY STUDY OF NITROGEN TETROXIDE AND THE Ti-6Al-4V ALLOY[a,b]

Number	Reaction	Standard Heat of Reaction, ΔH_R°, kcal		Standard Free Energy of Reaction, ΔG_R°, kcal	
		298 K (77 F)	400 K (260 F)	298 K (77 F)	400 K (260 F)
	Group A. Changes of State or Reactions Between N_2O_4, NO, NO_2, O_2, and H_2O				
1 *	$N_2O_4(g) \rightleftharpoons N_2O_4(\ell)$	-6.846	-5.177	-0.073	+1.988
2 §	$3N_2O_4(\ell) + 2H_2O(\ell) \rightleftharpoons 4HNO_3(\ell) + 2NO(g)$	+28.432	–	+8.868	–
3 §	$2N_2O_4(\ell) + H_2O(\ell) \rightleftharpoons 2HNO_3(\ell) + NO(g) + NO_2(g)$	+24.374	–	+5.040	–
4 §	$N_2O_4(\ell) + \frac{1}{2}O_2(g) \rightleftharpoons N_2O_5(g)$	+7.376	+5.852	+4.904	+4.29
5 *	$N_2O_4(\ell) + \frac{1}{2}O_2(g) + H_2O(\ell) \rightleftharpoons 2HNO_3(\ell)$	-9.702	–	-4.622	–
6 *	$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons \frac{1}{2}N_2O_4(\ell)$	-23.198	-23.161	-9.056	-4.091
7 *	$2NO_2(g) \rightleftharpoons N_2O_4(\ell)$	-20.946	-18.682	-1.212	+5.105
	Group B. Reactions of Elemental Ti, Al, and V with N_2O_4				
8 §	$Ti(c) + \frac{1}{2}N_2O_4(\ell) \rightleftharpoons TiO_2(c) + \frac{1}{2}N_2(g)$	-223.162	-223.870	-223.924	-224.084
9	$Ti(c) + \frac{1}{2}N_2O_4(g) \rightleftharpoons TiO_2(c) + \frac{1}{2}N_2(g)$	-226.585	-226.409	-223.961	-223.090
10 §	$Ti(c) + \frac{1}{4}N_2O_4(\ell) \rightleftharpoons TiO(c) + \frac{1}{4}N_2(g)$	-122.731	-123.052	-122.713	-122.657
11	$Ti(c) + \frac{1}{4}N_2O_4(g) \rightleftharpoons TiO(c) + \frac{1}{4}N_2(g)$	-124.443	-124.347	-122.731	-122.160
12 §	$Ti(c) + \frac{1}{2}N_2O_4(\ell) \rightleftharpoons TiN(c) + O_2(g)$	-78.162	-78.920	-85.278	-87.596
13 §	$Ti(c) + \frac{1}{2}N_2O_4(g) \rightleftharpoons TiN(c) + O_2(g)$	-81.585	-81.509	-85.315	-86.602
14	$2Ti(c) + \frac{1}{2}N_2O_4(\ell) \rightleftharpoons TiN(c) + TiO_2(c)$	-303.662	-304.361	-297.561	-295.376
15 §	$2Ti(c) + \frac{3}{4}N_2O_4(\ell) \rightleftharpoons Ti_2O_3(c) + \frac{3}{4}N_2(g)$	-359.393	-360.254	-359.686	-359.649
16	$2Ti(c) + \frac{3}{4}N_2O_4(g) \rightleftharpoons Ti_2O_3(c) + \frac{3}{4}N_2(g)$	-364.528	-364.137	-359.740	-358.158
17	$Ti(c) + \frac{1}{2}N_2O_4(g) \rightleftharpoons TiO_2(c) + \frac{1}{2}N_2(g)$	-226.580	-226.409	-223.958	-223.089
18 §	$2Al(c) + \frac{3}{4}N_2O_4(\ell) \rightleftharpoons Al_2O_3(c) + \frac{3}{4}N_2(g)$	-396.893	-398.198	-395.540	-394.873
19	$2Al(c) + \frac{3}{4}N_2O_4(g) \rightleftharpoons Al_2O_3(c) + \frac{3}{4}N_2(g)$	-402.028	-402.081	-395.594	-393.382
20 §	$2V(c) + \frac{3}{4}N_2O_4(\ell) \rightleftharpoons V_2O_3(c) + \frac{3}{4}N_2(g)$	-292.493	-293.243	-294.431	-292.605
21	$2V(c) + \frac{3}{4}N_2O_4(g) \rightleftharpoons V_2O_3(c) + \frac{3}{4}N_2(g)$	-297.628	-297.126	-294.486	-291.114
22 *	$V(c) + \frac{1}{2}N_2O_4(\ell) \rightleftharpoons VN(c) + 2O_2(g)$	-38.462	-39.229	-46.191	-48.703
23 §	$Al(c) + \frac{1}{2}N_2O_4(g) \rightleftharpoons AlN(c) + 2O_2(g)$	-77.085	-77.167	-80.272	-81.348
24	$7/2\,V(c) + \frac{3}{4}N_2O_4(\ell) \rightleftharpoons 3/2\,VN(c) + V_2O_3(c)$	-353.693	-354.368	-346.257	-341.205
25	$7/2\,Al(c) + \frac{3}{4}N_2O_4(\ell) \rightleftharpoons 3/2\,AlN(c) + Al_2O_3(c)$	-510.893	-512.242	-498.432	-493.930
	Group C. Reactions of Elemental Ti, Al, and V with N_2O_4 Impurities				
26	$Ti(c) + 2N_2O(g) \rightleftharpoons TiO_2(c) + 2N_2(g)$	-264.720	-264.451	-262.075	-261.212
27	$Ti(c) + \frac{1}{2}N_2O(g) \rightleftharpoons TiN(c) + \frac{1}{2}O_2(g)$	-90.305	-90.256	-86.085	-84.650
28	$Ti(c) + N_2O(g) \rightleftharpoons TiO(c) + N_2(g)$	-143.510	-143.368	-141.788	-141.221
29 *	$Ti(c) + NO(g) \rightleftharpoons TiO(c) + \frac{1}{2}N_2(g)$	-145.480	-145.428	-137.589	-134.899
30 *	$Ti(c) + 2NO(g) \rightleftharpoons TiO_2(c) + N_2(g)$	-268.660	-268.57.	-253.677	-248.568
31 *	$Ti(c) + NO(g) \rightleftharpoons TiN(c) + \frac{1}{2}O_2(g)$	-102.080	-102.081	-94.334	-91.686
32 *	$Ti(c) + \frac{1}{2}NO_2(g) \rightleftharpoons TiO(c) + \frac{1}{4}N_2(g)$	-127.855	-127.723	-123.016	-121.380
33 *	$Ti(C) + NO_2(g) \rightleftharpoons TiO_2(c) + \frac{1}{2}N_2(g)$	-233.410	-233.161	-224.530	-221.351
34	$Ti(c) + NO_2(g) \rightleftharpoons TiN(c) + O_2(g)$	-88.410	-88.261	-85.884	-85.043
35	$Ti(c) + NOCl(g) \rightleftharpoons TiCl_2 + 2NO(g)$	-105.580	-105.208	-103.674	-103.082
36 *	$5/2\,Ti(c) + NOCl(g) \rightleftharpoons \frac{1}{2}TiCl(c) + TiN(c) + TiO(c)$	-278.770	-278.523	-263.063	-257.732
37 *	$5/2\,V(c) + NOCl(g) \rightleftharpoons \frac{1}{2}VCl_2(c) + VN(c) + VO(c)$	-209.920	-209.427	-193.949	-189.774
38 *	$5/3\,Al(c) + NOCl(g) \rightleftharpoons 1/3\,AlCl_3(c) + AlN(c) + 1/3\,Al_2O_3(c)$	-278.090	-278.133	-260.699	-254.744
39 *	$Ti(c) + 2/3\,NO_3(g) \rightleftharpoons TiO_2(c) + 1/3\,N_2(g)$	-236.822	-236.591	-230.761	-228.625
40	$Ti(c) + 1/5\,N_2O_5(g) \rightleftharpoons TiO(c) + 1/5\,N_2(g)$	-124.400	-124.380	-122.529	-121.885
41 *	$Ti(c) + \frac{1}{4}N_2O_4(\ell) + \frac{1}{2}O_2(g) \rightleftharpoons TiO_2(c) + \frac{1}{4}N_2(g)$	-224.330	-224.605	-218.103	-215.932
42 *	$Ti(c) + \frac{1}{4}N_2O_4(g) + \frac{1}{2}O_2(g) \rightleftharpoons TiO_2(c) + \frac{1}{4}N_2(g)$	-226.040	-225.900	-218.122	-215.435
43 *	$Ti(c) + \frac{1}{4}N_2O_4(\ell) + NO(g) \rightleftharpoons TiO_2(c) + \frac{3}{4}N_2(g)$	-245.910	-246.195	-238.800	-236.326
44 *	$Ti(c) + \frac{1}{4}N_2O_4(g) + NO(g) \rightleftharpoons TiO_2(c) + \frac{3}{4}N_2(g)$	-247.620	-247.490	-238.819	-235.829
45 §	$Ti(c) + \frac{1}{4}N_2O_4(\ell) + H_2O(\ell) \rightleftharpoons TiO_2(c) + \frac{1}{4}N_2(g) + H_2(g)$	-155.980	–	-161.383	–
46 §	$Ti(c) + \frac{1}{4}N_2O_4(g) + H_2O(\ell) \rightleftharpoons TiO_2(c) + \frac{1}{4}N_2(g) + H_2(g)$	-157.720	–	-161.402	–
47	$2Ti(c) + \frac{1}{2}N_2O_4(\ell) + \frac{1}{2}O_2(g) \rightleftharpoons Ti_2O_3(c) + \frac{1}{2}N_2(g)$	-360.560	-360.090	-353.865	-351.498

TABLE A-2. (Continued)

Number	Reaction	Standard Heat of Reaction, ΔH_R°, kcal 298 K (77 F)	400 K (260 F)	Standard Free Energy of Reaction, ΔG_R°, kcal 298 K (77 F)	400 K (260 F)
48 *	$2Ti(c) + \frac{1}{2}N_2O_4(g) + \frac{1}{2}O_2(g) \rightleftharpoons Ti_2O_3(c) + \frac{1}{2}N_2(g)$	-363.965	-363.630	-353.892	-350.504
49	$2Ti(c) + \frac{1}{2}N_2O_4(\ell) + NO(g) \rightleftharpoons Ti_2O_3(c) + N_2(g)$	-382.140	-381.680	-374.562	-371.892
50 *	$2Ti(c) + N_2O_4(g) + NO(g) \rightleftharpoons Ti_2O_3(c) + N_2(g)$	-385.565	-385.220	-374.589	-370.898
51 §	$2Ti(c) + \frac{1}{2}N_2O_4(\ell) + H_2O(\ell) \rightleftharpoons Ti_2O_3(c) + \frac{1}{2}N_2(g) + H_2(g)$	-292.240	-	-297.145	-
52 §	$2Ti(c) + \frac{1}{2}N_2O_4(g) + H_2O(\ell) \rightleftharpoons Ti_2O_3(c) + \frac{1}{2}N_2(g) + H_2(g)$	-295.655	-	-297.172	-
53 *	$Ti(c) + \frac{1}{8}N_2O_4(\ell) + \frac{1}{4}O_2(g) \rightleftharpoons TiO(c) + \frac{1}{8}N_2(g)$	-123.315	-123.445	-119.802	-118.581
54 *	$Ti(c) + \frac{1}{8}N_2O_4(g) + \frac{1}{4}O_2(g) \rightleftharpoons TiO(c) + \frac{1}{8}N_2(g)$	-124.170	-124.092	-119.811	-118.332
55 *	$Ti(c) + \frac{1}{8}N_2O_4(\ell) + \frac{1}{2}NO(g) \rightleftharpoons TiO(c) + \frac{3}{8}N_2(g)$	-134.105	-134.240	-130.151	-128.778
56 *	$Ti(c) + \frac{1}{8}N_2O_4(g) + \frac{1}{2}NO(g) \rightleftharpoons TiO(c) + \frac{3}{8}N_2(g)$	-135.500	-134.890	-130.160	-128.529
57 §	$Ti(c) + \frac{1}{8}N_2O_4(\ell) + \frac{1}{2}H_2O(\ell) \rightleftharpoons TiO(c) + \frac{1}{8}N_2(g) + \frac{1}{2}H_2(g)$	-89.155	-	-91.442	-
58 §	$Ti(c) + \frac{1}{8}N_2O_4(g) + \frac{1}{2}H_2O(\ell) \rightleftharpoons TiO(c) + \frac{1}{8}N_2(g) + \frac{1}{2}H_2(g)$	-90.550	-	-91.451	-
59 *	$Ti(c) + N_2O_4(\ell) + 3NO(g) \rightleftharpoons TiO(NO_3)_2(c) + \frac{3}{2}N_2(g)$	-	-	-275.373	-
60	$Ti(c) + N_2O_4(\ell) + \frac{3}{2}O_2(g) \rightleftharpoons TiO(NO_3)_2(c)$	-	-	-213.282	-
	Group D. Reactions of TiO, and TiO_2, and TiN with N_2O_4 and Impurities in N_2O_4				
61	$TiO_2(c) + Ti(c) \rightleftharpoons 2TiO(c)$	-22.300	-22.285	-21.501	-21.230
62 *	$TiO(c) + \frac{1}{2}O_2(g) \rightleftharpoons TiO_2(c)$	-101.600	-101.553	-95.391	-93.275
63	$TiN(c) + \frac{1}{2}O_2(g) \rightleftharpoons TiO(c) + \frac{1}{2}N_2$	-43.400	-43.347	-43.255	-43.213
64 §	$TiO(c) + N_2O_4(\ell) \rightleftharpoons TiO_2(c) + 2NO(g)$	-53.764	-55.231	-77.241	-85.094
65 *	$TiO(c) + NO(g) \rightleftharpoons TiO_2(c) + \frac{1}{2}N_2(g)$	-123.180	-123.143	-113.780	-113.669
66	$TiO(c) + NO_2(g) \rightleftharpoons TiO_2(c) + NO(g)$	-87.930	-87.733	-86.941	-86.632
67 §	$TiO_2(c) + \frac{3}{2}N_2O_4(\ell) \rightleftharpoons TiO(NO_3)_2(c) + NO(g)$	-	-	+8.057	-
68 *	$TiO_2(c) + 3NO_2(g) \rightleftharpoons TiO(NO_3)_2(c) + NO(g)$	-	-	+6.239	-
69 *	$TiO_2(c) + 5NO(g) \rightleftharpoons TiO(NO_3)_2(c) + \frac{3}{2}N_2(g)$	-	-	-81.202	-
70 §	$TiN(c) + N_2O_4(\ell) \rightleftharpoons TiO(c) + 3NO(g)$	+25.778	+24.565	-4.446	-2.425
71 *	$TiO(c) + N_2O_4(\ell) + O_2(g) \rightleftharpoons TiO(NO_3)_2(c)$	-	-	-96.390	-
72 *	$TiO(c) + N_2O_4(\ell) + 2NO(g) \rightleftharpoons TiO(NO_3)_2(c) + N_2(g)$	-	-	-137.784	-
73 *	$TiO_2(c) + N_2O_4(\ell) + \frac{1}{2}O_2 \rightleftharpoons TiO(NO_3)_2(c)$	-	-	-0.999	-
74 *	$TiO_2(c) + N_2O_4(\ell) + NO(g) \rightleftharpoons TiO(NO_3)_2(c) + \frac{1}{2}N_2(g)$	-	-	-21.696	-
75	$TiO_2(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 2NO_2(g) + 2NO(g)$	+41.700	+42.360	+37.656	+34.123
76 *	$TiO_2(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 2N_2O_3(g)$	+22.320	+23.292	+38.416	+41.763
77 *	$TiO_2(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + \frac{3}{2}N_2O_4(\ell) + \frac{1}{2}N_2(g)$	-24.294	-20.803	+6.691	+14.744
78 §	$TiO_2(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 2N_2(g) + 3O_2(g)$	-17.280	-16.090	-28.232	-34.167
79 §	$TiO(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 3NO(g) + NO_2(g)$	-46.320	-45.103	-49.285	-50.509
80 §	$TiO(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 2N_2(g) + \frac{5}{2}O_2(g)$	-118.800	-117.643	-123.623	-125.442
81	$TiO(c) + 2NOCl(g) \rightleftharpoons TiCl_2(c) + NO_2(g) + NO(g)$	+4.650	+4.810	+4.768	+4.780
82	$TiN(c) + 4NOCl(g) \rightleftharpoons TiCl_4(c) + 3NO(g) + N_2O(g)$	-77.930	-76.690	-79.891	-80.757
83 *	$TiN(c) + 5NOCl(g) + 2H_2O(\ell) \rightleftharpoons TiCl_4(c) + NH_4Cl(c) + 3NO(g) + N_2O_4(\ell)$	-53.573	-	-32.857	-
84	$TiO_2(c) + 2HNO_3(\ell) \rightleftharpoons TiO(NO_3)_2(c) + H_2O(\ell)$	-	-	+3.621	-
85	$TiO(c) + 2HNO_3(\ell) \rightleftharpoons Ti(NO_3)_2(c) + H_2O(\ell)$	-	-	-28.768	-
	Group E. Reactions for Possible Cl Removal by Silver Additions				
86	$NOCl(g) + Ag(c) \rightleftharpoons AgCl(c) + NO(g)$	-21.402	-	-21.576	-
87 §	$N_2O_4(\ell) + Ag(c) \rightleftharpoons AgNO_3(c) + NO(g)$	-3.174	-	-10.275	-
88 §	$\frac{1}{2}N_2O_4(\ell) + 2Ag(c) \rightleftharpoons Ag_2O(c) + NO(g)$	+16.612	-	+6.470	-
89 *	$AgNO_3(c) + NOCl(g) \rightleftharpoons AgCl(c) + N_2O_4(\ell)$	-18.228	-	-11.301	-
90	$2AgCl(c) + Ti(c) \rightleftharpoons TiCl_2(c) + 2Ag(c)$	-62.776	-	-60.522	-

(a) The following notations are used in this table:

(g) designates gas phase

(c) designates condensed or solid phase

(ℓ) designates liquid phase

* designates reactions favored for completion by increasing pressure

§ designates reactions repressed by increasing pressure.

(b) Numerical values carried beyond the significant place for computational consistency.

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13. ABSTRACT

This memorandum summarizes information on the corrosion of titanium and its alloys available during the period 1960 to mid 1966. It describes the corrosion resistance of titanium in salt solutions, acids, gases, organic media and liquid metals. Included are such topics as field-service experiences, stress-corrosion cracking, galvanic (two-metal) coupling, and anodic protection for titanium and titanium alloys. Media in which stress-corrosion cracking is reported include NaCl solutions, H_2SO_4, HCl, dry red-fuming nitric acid, methanol containing H_2SO_4 or HCl, certain grades of N_2O_4, molten cadmium, mercury, silver and silver-containing compounds and alloys. Stress-corrosion cracking data on hot salt and accelerated crack propagation were covered previously in DMIC Technical Note, February 1, 1966.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
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Titanium alloys						
Corrosion						
Stress-corrosion cracking						
Galvanic corrosion						
Crevice corrosion						
Pitting corrosion						
Corrosion fatigue						
Cavitation						
Anodic Protection						
Field service						
Heat transfer						
Radiation exposure						
Noble metal additions						
Descaling						
Inhibitors						
Seawater						
Salt solutions						
Crude oil						
Sulfuric acid						
Hydrochloric acid						
Nitric acid						
Fuming-nitric acid						
Nitrogen tetroxide						
Phosphoric acid						
Mixed acids						
Chlorine						
Hydrogen						
Hydrogen sulfide						
Sulfur dioxide						
Sulfur trioxide						
Stack gases						
Ammonia						
Molten alkali						
Sodium fluoride						
Food						
Methyl alcohol solutions						
Organic chemicals						
Formic acid						
Oxalic acid						
Tall oil						
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