

UNCLASSIFIED

AD NUMBER
AD091121
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies only; Administrative/Operational Use; MAR 1956. Other requests shall be referred to Wright Air Development Center, Wright-Patterson AFB, OH 45433.
AUTHORITY
WADC per DTIC Form 55, 21 Sep 1990

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD 91121

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON 2, OHIO

This document is the property of the United States Government. It is furnished for the duration of the contract and shall be returned when no longer required, or upon recall by ASTIA to the following address: Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio.

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION, THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

PROGRESS REPORT NO. 26-4

AD NO. 91221
ASTIA FILE COPY

CORROSION AND IGNITION OF TITANIUM ALLOYS IN
FUMING NITRIC ACID

IV. STUDY OF ADDITIONAL TITANIUM ALLOYS

JOHN B. RITTENHOUSE
JULIA S. WHITTICK

FC

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 3, CALIFORNIA
MARCH 30, 1956

Contract No. AF 33(616)-3066
Department of the Air Force

Progress Report No. 26-4

CORROSION AND IGNITION OF TITANIUM ALLOYS IN FUMING NITRIC ACID
IV. STUDY OF ADDITIONAL TITANIUM ALLOYS

John B. Rittenbouse
John S. Whittick

David Altman
David Altman, Chief
Chemistry and Physics Section

Arthur J. Stosiek
Arthur J. Stosiek, Chief
Rockets and Materials Division

W. H. Pickering
W. H. Pickering, Director
Jet Propulsion Laboratory

Copy No. 34

JET PROPULSION LABORATORY
California Institute of Technology
Pasadena 3, California
March 30, 1956

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

The information furnished herewith is made available for study upon the understanding that the Government's proprietary interests in and relating thereto shall not be impaired. It is desired that the Judge Advocate (RCJ), Wright Air Development Center, Wright-Patterson, Air Force Base, Ohio, be promptly notified of any apparent conflict between the Government's proprietary interests and those of others.

This document may not be reproduced or published in any form in whole or part without prior approval of the Government. Since this is a progress report the information herein is tentative and subject to changes, corrections, and modifications.

TABLE OF CONTENTS

	Page
I. Introduction ..	i
II. Experimental Procedure	2
III. Results	2
A. Corrosion-Time Curves of Ti-8% Mn Alloy ..	2
B. Corrosion Rates of Some Titanium Alloys ..	5
C. Thirty-Day Storage Tests of Some Titanium Alloys in Thermally Stable FNA at 30°C ..	6
D. Effect of Polishing Titanium Samples in Argon Atmosphere on Corrosion in Anhydrous FNA (20% NO ₂)	7
IV. Summary	7
V. Work in Progress	8
Tables	9
Figures	14
References ..	19

LIST OF TABLES

I. Chemical Analysis of Titanium Alloys	9
II. Corrosion of Vacuum Stress Relieved and Sandblasted Ti-8% Mn Alloy in Anhydrous FNA (20% NO ₂) at Ambient Temperature	10
III. Average Corrosion Rates of Sandblasted Titanium Alloys Stored for One Week in FNA at 30°C ..	11
IV. 30-Day Corrosion Tests at 30°C of Titanium Alloys in FNA (13% NO ₂ and 2% H ₂ O)	12
V. Effect of Polishing in Argon Atmosphere on Corrosion of Titanium in Anhydrous FNA (20% NO ₂)	13

LIST OF FIGURES

	Page
1. Log-Log Plot of Corrosion of Vacuum-Stress-Relieved and Sandblasted Ti-8% Mn Alloy in Anhydrous FNA (20% NO ₂) at Ambient Temperature	14
2. Corrosion of Vacuum-Stress-Relieved and Sandblasted Ti-8% Mn Alloy in Anhydrous FNA (20% NO ₂) at Ambient Temperature	14
3. Average Corrosion Rates of Vacuum-Stress-Relieved and Sandblasted Ti-8% Mn Alloy in Anhydrous FNA (20% NO ₂) at Ambient Temperature	15
4. Average Corrosion Rates of Sandblasted Commercially Pure Titanium A55 in FNA at 30°C for 1 Week	15
5. Average Corrosion Rates of Sandblasted Commercially Pure Titanium Ti 100A in FNA at 30°C for 1 Week	16
6. Average Corrosion Rates of Sandblasted Titanium Alloy Ti 140A in FNA at 30°C for 1 Week	16
7. Average Corrosion Rates of Sandblasted Titanium-6% Aluminum-4% Vanadium Alloy in FNA at 30°C for 1 Week	17
8. Average Corrosion Rates of Sandblasted Titanium Alloy A110 AT in FNA at 30°C for 1 Week	17
9. Sheared Edge of Titanium-6% Aluminum-4% Vanadium Alloy after Storage for 1 Week at 30°C in Anhydrous FNA (20% NO ₂) (Approx. 20X)	18
10. Photomicrograph of Edge of Sample of Fig. 9 (150X)	18

ABSTRACT

The corrosion-time curve of the titanium-8% manganese alloy follows initially a power-function law; a linear law is followed in the later stages of corrosion. Corrosion rates, ignition sensitivity, and stress corrosion cracking of titanium alloys A55, Ti 100A, Ti 140A, Ti 6 Al-4V, and A 110AT were studied. Storage tests for thirty days at 30°C of several titanium alloys in thermally stable fuming nitric acid (13% NO_2 -2% H_2O) were completed.

I. INTRODUCTION

Bomberger (Cf. Ref. 1) reviewed the literature on the corrosion of titanium in various acids, but there was little work done on the corrosion of alloys of titanium. Most of the corrosion work reviewed was concerned with commercially pure titanium. Kiefer and Hoyle (Cf. Ref. 2) did some work on the stress-corrosion cracking of commercially pure titanium, and Ti 140A (Cr, Fe, Mo alloy) was briefly mentioned. There are other alloys of titanium which will be of interest in aircraft and missile applications because of mechanical properties of fabrication of the material. The corrosion, ignition sensitivity, and stress-corrosion cracking susceptibility of some of these alloys after storage in fuming nitric acid (FNA) will be studied. Chemical analyses of the alloys studied are shown in Table I.

The form of the corrosion-time curve is of importance if an understanding of the corrosion mechanism is to be gained. The nature of the corrosion-time curve of a material in a given environment at a definite temperature is also of importance when one wishes to compare corrosion rates of materials for long periods of storage. When the corrosion-time curve of a material in a given environment is linear, that is, the corrosion rate is constant, then corrosion rates can be extrapolated with some expectation of accuracy. There is some danger in extrapolating corrosion rates over too long a period of storage even when the corrosion-time curve is linear, however, there is even greater possibility for error in extrapolation if the corrosion behavior of a material follows a power function or an exponential corrosion-time curve. Phenomena which reduce the reliability of extrapolation are

pitting or intergranular corrosion altering the cross section of a material in localized areas. These factors would not be reflected in ordinary corrosion data obtained by the conventional weight-loss method. For these reasons, it has been the general practice to conduct fairly long-term exposure tests to ascertain the extent and nature of the corrosion. It is also best to expose the material to the corrosion environment of greatest practical interest for the application at hand. Accordingly, 30-day-exposure tests of several titanium alloys were conducted at 30 °C using FNA specification M11-N-7254A Type III (13% NO_2 and 2% H_2O).

II. EXPERIMENTAL PROCEDURE

The data for the corrosion-time curve of the titanium-8% manganese alloy were obtained by the conventional weight-loss method. The samples were supported on glass hooks and stored in glass tubes about 1 inch in diameter with a ground tapered joint to which was fitted a stopcock with a smaller ball-joint tube, the lower end of the 1-inch-diameter tube was drawn out and fitted with a stopcock for drainage while a side arm tube was provided with a stopcock in order to evacuate the assembly. Similar equipment was used for the storage tests in FNA of various compositions and for the 30-day storage tests.

Samples of commercially pure titanium and the alloy containing 8% manganese were polished on metallographic polishing paper in a dry box under an argon atmosphere. The polishing was carried to 500-grit-size abrasive paper. After polishing, the samples were cleaned with solvent and weighed in argon-filled bottles. After weighing, the samples were returned to the dry box and inserted into the storage apparatus; the FNA was added to the equipment while under an argon atmosphere.

III. RESULTS

A. Corrosion Time Curves of Ti-8% Mn Alloy

Vacuum-stress-relieved and sandblasted samples of titanium-8% manganese alloy were exposed to anhydrous FNA (20% NO_2) for periods of time ranging from 1 to 163 hours at ambient temperature. The extent of corrosion was obtained in grams/cm² and converted to mils by use of suitable conversion units.

The extent of corrosion was plotted against time on log-log coordinates to determine whether or not the corrosion followed any of the experimental corrosion laws discussed by Evans (Cf. Ref. 3). In Figure 1 it can be seen that the experimental points fall reasonably well on a straight line on log-log coordinates during the initial period of corrosion. For the period of 1 to approximately 30 hours it appears that the corrosion follows a power-function law of the form

$$w = K_1 t^n \quad (1)$$

where w = extent of corrosion in mils, K_1 and n are constants characteristic of the corrosion environment, the temperature, and the metal involved, and t = time in hours. Under the conditions of this experiment and in the above units, $K_1 = 0.043$ and $n = 0.63$.

During the period of time from 30 to 160 hours, the experimental data deviate from the initial straight line on log-log coordinates as can be seen in Figure 1. When these data are plotted on rectangular coordinates in Figure 2, it can be seen that the corrosion curve from approximately 30 to 160 hours follows a straight line indicating a curve of the form:

$$w = K_2 t \quad (2)$$

The constant K_2 for the straight line portion of Figure 2 has the value 0.0125 mils/hr.

It is interesting to note that the initial stage of corrosion of the titanium-8% manganese alloy follows a power-function law similar to that of the commercially pure titanium. This behavior indicates that initially the corrosion reaction is diffusion-controlled. When the film reaches a critical thickness (i.e., in approximately 20 to 30 hours) the additional corrosion product no longer presents an adherent film to contact of the FNA with the metal surface. As discussed in the previous report (Cf. Ref. 4), it was stated that for a truly adherent film where the mechanism is diffusion-controlled, the parabolic law yielding a time exponent of 0.5 should result. However, for a porous film with random cracks, the corrosion approximates the linear law. It would be reasonable to conclude, therefore, that in the initial phase, the corrosion product is largely flawless and adherent; but that after about 30 hours, additional corrosion forms a loose or porous product offering little corrosion resistance.

The average corrosion rates over a time interval t were computed from the corrosion-time data by dividing the extent of corrosion at that time by t . These data are plotted on rectangular coordinates in Figure 3. If the corrosion in the later periods of time were truly linear, then the curve in Figure 3 from 30 to 160 hours should be a horizontal line. It can be seen that this is not quite true. There is a slight downward slope to the plot indicating that additional corrosion increases the resistance only slightly. The mean value of the corrosion rate, however, from 30 to

160 hours is 106 mils/yr, and the deviation of the points from this mean value between the limits of 30 and 160 hours is 1.4%. This mean value of 106 mils/yr is in fair agreement with the corrosion rate of 104 mils/yr found for this alloy previously (Cf. Ref. 4). In the case of a linear corrosion law, the average corrosion rate $\bar{R}$ is equal to the instantaneous corrosion rate $\dot{w}$; however, in a power-function law the instantaneous rate is not equal to the average corrosion rate, these relationships are shown as follows:

$$w = K_1 t^n \quad \text{power-function law} \quad (3)$$

$$\bar{R} = \frac{w}{t} = K_1 t^{n-1} \quad \text{average corrosion rate} \quad (4)$$

$$\dot{w} = \frac{dw}{dt} = nK_1 t^{n-1} \quad \text{instantaneous corrosion rate} \quad (5)$$

$$w = K_2 t \quad \text{linear law} \quad (6)$$

$$\bar{R} = \frac{w}{t} = K_2 \quad \text{average corrosion rate} \quad (7)$$

$$\dot{w} = \frac{dw}{dt} = K_2 \quad \text{instantaneous corrosion rate} \quad (8)$$

In the initial stages of corrosion of the titanium-8% manganese alloy the corrosion is largely diffusion-controlled until after about 25 to 30 hours during which time finely divided titanium is accumulated on the metal surface by the process of selective chemical attack on the manganese-rich areas. At this state in the corrosion process the corrosion rate becomes constant, indicating that the surface coating is offering a constant resistance to access of the corrosive medium. It should be mentioned that all of the samples were sensitive to ignition reactions after removal from the acid, drying, and then probing after moistening with a drop of red fuming nitric acid. This ignition sensitivity is considered to result from the accumulation of the finely divided titanium formed in the early stages of corrosion.

The corrosion data are tabulated in Table II, as are data of the acid decomposition. In general the NO_2 and the H_2O concentrations increase with time. There are some inconsistencies in these data which can be traced to two sources: (1) the apparatus in which the samples were stored was not sealed so that leakage of NO_2 or H_2O vapor was possible, and (2) there are no corrections made in the analysis for the metals in solution in the acid. This factor would have its greatest effect upon the H_2O determination since the latter is determined by difference. The total metals in solution in the acid average between 0.04 and 0.08%; this amount of metal salts

may or may not influence the acid analysis, but, since the valence state of the titanium in the acid solution is not known precisely, corrections to the acid analysis for metal-salt content cannot be applied with certainty.

B. Corrosion Rates of Some Titanium Alloys

The average corrosion rates of several titanium alloys of commercial importance which can be obtained in sheet form are shown in Table III and in Figures 4 through 8.

In general the corrosion rates of these titanium alloys as a function of the NO_2 and H_2O concentrations of the FNA are comparable to the behavior of the commercially pure titanium and the titanium-8% manganese alloy. That is, the corrosion rates increase with increasing NO_2 concentrations in the range 0 to 20% NO_2 , and the corrosion rates decrease with increasing H_2O concentrations in the range 0 to 2%.

The ignition-sensitivity behavior of the several alloys was similar to the behavior of the commercially pure titanium and the titanium-8% manganese alloy. All of the alloys were ignition sensitive after exposure to anhydrous FNA containing 10 and 20% NO_2 , although the ignition tendencies were lower with exposure to FNA containing the lower concentration of NO_2 . This was particularly true of the A55 and Ti 140A alloys. The 6 Al-4V and A 110AT alloys were nearly as ignition sensitive as the C 110M alloy after exposure to 20% NO_2 FNA. The 6 Al-4V and the A 110AT alloys exhibited slight ignition sensitivity in the anhydrous FNA without NO_2 . None of the alloys was sensitive to ignition reactions when stored in FNA of concentrations of 0 to 20% NO_2 and 1 to 2% H_2O .

It is interesting to compare corrosion rates of the several alloys in anhydrous FNA (20% NO_2) because it is in this solution that the largest rates are obtained. The highest rate is that of the titanium-8% manganese alloy; however, the two alloys containing aluminum (i.e., Ti 6 Al-4V and A 110AT) exhibit relatively high corrosion rates in FNA of this composition. Attention should be called to the comparatively low corrosion rate of the chromium, iron, molybdenum alloy Ti 140A in acid of this composition. This alloy exhibits the lowest corrosion rates of any of the alloys tested. The high corrosion rate of the 6 Al-4V alloy in FNA containing no NO_2 and H_2O should also be noted; this rate of 1 mil per year is the highest rate in acid of this composition found for any of the alloys.

The relatively high corrosion rates of the commercially pure alloy Ti 100A are particularly interesting when compared with the low corrosion rates of the two other commercially pure alloys A55 and Ti 75A. Chemically the only difference between the A55, Ti 75A alloys and the Ti 100A material is the higher iron content of the latter (Cf. Table I). Comparison of the corrosion rates of the Ti 100A alloy with the Ti 140A alloy (Cf. Table III and Fig. 5 and 6) is impressive inasmuch

as the iron content of the Ti 140A alloy is 10 times that of the Ti 100A (Cf. Table I), yet the corrosion rates of the former are considerably lower.

All of the alloys tested were susceptible to stress corrosion cracking in anhydrous FNA containing 20% NO_2 (Cf. Figs. 4 through 8). The two alloys containing aluminum (Cf. Figs. 7 and 8) and the Ti 75A and C 110M (Cf. Ref. 5) were susceptible to stress corrosion cracking in anhydrous FNA with 10% NO_2 . Only the 6 Al-4V alloy (Cf. Fig. 7) and C 110M (Cf. Ref. 5) material were susceptible to stress corrosion cracking in FNA containing no NO_2 or H_2O .

The stress corrosion cracks in the Ti 100A and the 6 Al-4V alloy originated in the sheared edges as can be seen in the photograph of Figure 9. The complex nature of the stress corrosion cracking and the fact that the cracks probably originated in the sheared edges is shown in the photomicrograph of Figure 10.

C. Thirty-Day Storage Tests of Some Titanium Alloys in Thermally Stable FNA at 29°C

Storage tests for 30 days at 30°C of several titanium alloys were conducted with Laboratory prepared FNA of a composition conforming to specification Mil-N-7254A Type III containing 13% NO_2 and 2% H_2O . The results of these tests are shown in Table IV. It is interesting to note that the Ti 6 Al-4V alloy had the highest corrosion rate under these conditions. According to the criterion of Hildebrandt (Cf. Ref. 6) all of these alloys would be considered perfectly resistant to corrosion. Hildebrandt's terminology converted to mils per year is as follows.

Perfect Resistance	1 to 4 mils/yr
Adequate Resistance	4 to 12 mils/yr
Moderate Resistance	12 to 40 mils/yr
Little Resistance	40 to 80 mils/yr
Not Resistant	> 80 mils/yr

The question of importance, however, is whether or not these alloys are susceptible to stress-corrosion cracking and ignition reactions after exposure to FNA of this composition.

Examination of the duplicate samples under 10 times magnification disclosed no stress-corrosion cracking around sheared edges or stamped-in identification numbers. Probing tests of the samples after moistening with fresh acid resulted in no ignition reactions. It would be desirable to conduct longer term tests of some of these alloys in FNA of this composition to determine whether there is sensitivity toward ignition reaction or susceptibility to stress-corrosion cracking during longer term storage.

D. Effect of Polishing Titanium Samples in Argon Atmospheres on Corrosion in Anhydrous FNA (20% NO_2)

Samples of commercially pure titanium and the titanium-8% manganese alloy were processed for FNA storage in an argon atmosphere in order to prevent contact of the freshly prepared metal surface with the oxygen and nitrogen of the air. It is known that titanium reacts with both the oxygen and nitrogen of the air. The reaction rate at room temperature with nitrogen is slower than that for oxygen, however, there is a thin oxide film formed on freshly cleaned titanium surfaces at room temperature (Cf. Ref. 7). In Table V the extent of corrosion of the titanium samples thus prepared are compared with the data obtained with samples that had been sandblasted in air. There is a significant increase in the corrosion of those samples that were polished in the inert atmosphere. The extent of corrosion of samples that were polished in air (Cf. Table V) is less than that of samples polished in the inert atmosphere, which is an indication of the probable formation of an oxide film on the freshly polished surface which has been exposed to air. This film serves as a temporary barrier to extensive corrosion. The explanation for the smaller percent increase in corrosion of the sandblasted commercially pure titanium (Ti 75A) specimens over the inert atmosphere polished samples as compared with the titanium-8% manganese alloys (C 110A) in parallel condition is probably due to the fact that corrosion in the commercially pure titanium is in the small randomly located intergranular sites, while in the titanium-8% manganese alloy the corrosion attack is selective on the larger beta-phase areas containing the alloying elements in solid solution (Cf. Ref. 5).

The rather large increase in corrosion of the stress-relieved titanium-8% manganese alloy samples that were polished in argon is probably due to two factors. First, the relatively thicker oxide layer formed during the metal processing (i.e., rolling, pickling) is absorbed at the stress-relieving temperature (475°C) (Cf. Ref. 7). As the heat-treatment was conducted in a vacuum, a fairly thin layer is probably formed after exposure to the air. This thinner oxide film, offers less of a barrier to corrosion than the one on the metal formed during processing, and therefore a higher corrosion rate results for the vacuum-stress-relieved and inert-gas-polished sample. Secondary effects may also result from the fact that stress-relieving possibly redistributes the alloying element (manganese in this case) by solid-state diffusion in the beta phase in such a way that a more uniform alloy-element distribution results.

IV. SUMMARY

The titanium-8% manganese alloy corrosion-time curve obtained at ambient temperature in anhydrous FNA (20% NO_2) exhibits a transition from power-functional behavior over the first 25 to 30 hours of storage to a linear behavior with constant corrosion rate over a period starting at approximately 30 hours to 160 hours of storage.

Thirty-day storage tests were completed of several titanium alloys at 30°C in Type III FNA (13% NO_2 and 2% H_2O). The corrosion was negligible for all of the alloys tested, there was no ignition sensitivity exhibited by any of the samples, nor was there any susceptibility to stress corrosion cracking. The highest corrosion rate was observed for the Ti-6Al-4V alloy, while the lowest rates were found for the commercially pure titanium (A55, Ti 75A) and for the chromium, iron, molybdenum alloy Ti 140A.

Samples of commercially pure titanium and the alloy containing 8% manganese were polished in an inert atmosphere and stored in anhydrous FNA (20% NO_2) for one week at ambient temperature. The extent of corrosion of specimens thus prepared was 30 to 40% higher than the corrosion of samples that had been sandblasted before storage. This behavior indicates that, although sandblasting no doubt removes the oxide film which results from normal metal processing, another, possibly thinner, oxide film forms on the freshly cleaned metal surface after only short-time exposure to air at room temperature.

V. WORK IN PROGRESS

Elevated-temperature storage tests of titanium and titanium alloys in FNA of various compositions using teflon-lined, sealed pressure vessels is proceeding. This work will include studies of ignition sensitivity, stress-corrosion cracking, and corrosion rates of the material.

TABLE I
Chemical Analysis of Titanium Alloys

Alloy	C	N ₂	Fe	Mn	Al	Cr	H ₂	V	Ti
A 55 ^a	< 0.1	0.04	-	-	-	-	98 ^b	-	-
Ti 75A ^c	0.031	0.021	0.083	-	-	-	0.007	-	99.6
Ti 100A ^c	0.034	0.020	0.183	-	-	-	0.008	-	99.3 ^d
Ti 140A ^c	0.024	0.024	1.81	Mo 1.49	-	1.79	0.015	-	93.7 ^d
Ti-6Al-4V ^c	0.02	0.019	0.11	-	6.1	-	0.015	4.2	89.5 ^d
A 110AT ^a	< 0.1	0.03	-	-	5.0	-	94 ^b	Sn 3.0	-
C 110M ^a	< 0.1	0.02	-	8.5	-	-	86 ^b	-	-

^aItem Cru Titanium, Inc.

^bParts per million.

^cTitanium Metals Corp. of America.

^dApproximate.

TABLE II
Corrosion of Vacuum-Stress-Relieved and Sandblasted Ti-8% Mn Alloy
in Anhydrous FNA (20% NO₂) at Ambient Temperature

Time (hrs)	Corrosion (mils)	Corrosion Rate (mils/yr)	Acid Decomposition	
			NO ₂ (wt %)	H ₂ O ^b (wt %)
1	0.043	377	20.52 ± 0.03 ^a	0.06 ± 0.06 ^a
2	0.056	244	20.74 ± 0.02	0.11 ± 0.08
4	0.093	203	20.67 ± 0.02	0.04 ± 0.03
16	0.21	116	20.74 ± 0.01	0.14 ± 0.07
20	0.28	121	20.78 ± 0.03	0.14 ± 0.09
25	0.29	102	20.92 ± 0.01	0.26 ± 0.10
30	0.35	101	21.04 ± 0.04	0.26 ± 0.11
54	0.64	103		
69	0.89	113	21.15 ± 0.05	0.86 ± 0.11
90	1.13	110	21.28 ± 0.02	0.43 ± 0.05
120	1.51	110	21.58 ± 0.08	0.57 ± 0.11
160	1.92	104		
0	-	-	20.57 ± 0.01	0.07 ± 0.07
168 ^c	-	-	20.08 ± 0.04	0.12 ± 0.09

^aThe average deviation of two determinations.

^bWt % H₂O determined by subtracting sum of Wt % HNO₃ plus Wt % NO₂ from 100%.

^cBlank.

TABLE III
Average Corrosion Rates* of Some Sandblasted Titanium Alloys Stored for One Week in FNA at 30°C

Alloy	0% NO ₂			10% NO ₂			20% NO ₂		
	H ₂ O (%)			H ₂ O (%)			H ₂ O (%)		
	0	1	2	0	1	2	0	1	2
A 55	0.175	0.177	0.207	0.231	0.220	0.188	8.8	0.204	0.195
Ti 75A ^b	0.133	0.130	0.115	0.440	0.225	0.165	4.77	0.142	0.187
Ti 100A	0.732	0.416	0.253	1.00	0.293	0.280	21.60	0.305	0.340
Ti 140A	0.210	0.155	0.085	0.377	0.196	0.248	2.47	0.220	0.175
Ti 6Al-4V	1.06	0.310	0.235	7.55	0.618	0.511	29.65	0.396	0.436
A 110AT	0.640	0.183	0.146	6.40	0.275	0.303	43.1	2.54	0.317
C 110N ^b	0.317	0.165	0.204	12.5	0.212	0.165	72.1	0.105	0.155

*Corrosion rates in mils/yr.

^bTables II and V of Ref. 3.

TABLE IV
30-Day Corrosion Tests at 30°C of Titanium Alloys in FNA
(13% NO₂ and 2% H₂O)

Alloy	Corrosion (mils)
A 55 ^a	0.0038
Ti 75A ^a	0.0035
Ti 75A ^b	0.0031
Ti 100A ^a	0.0052
C 110W ^a	0.0052
C 110M ^b	0.0054
A 110AT ^a	0.0078
Ti 149A ^a	0.0039
Ti 6 Al-4V ^a	0.0164

^aAll samples as received and sandblasted.

^bSamples vacuum stress relieved and sandblasted.

TABLE V
Effect of Polishing in Argon Atmosphere on Corrosion of Titanium
in Anhydrous FNA (20% NO₂)

Alloy	Average Corrosion (mils)	Change in Corrosion (%)	Condition	
Ti 75A	0.116	+32 ^c	As received and polished in Argon	2
Ti 75A	0.088 ^a	-	As received and sandblasted	1
Ti 75A	0.106 ^b	+17 ^c	As received and polished in Air	3
C 110M	1.34 ^a	-	As received and sandblasted	1a
C 110M	0.680 ^b	-69 ^d	As received and polished in Air	3a
C 110M	1.86	+40 ^d	As received and polished in Argon	2a
C 110M	2.78	+107 ^d	Stress-relieved and polished in Argon	4a

^aComputed from data of Ref. 4.

^bComputed from data of Ref. 5

^cCondition 1 used as basis.

^dCondition 1a used as basis.

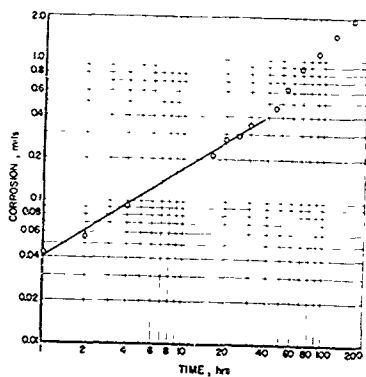


Figure 1
Log-Log Plot of Corrosion of Vacuum-
Stress-Relieved and Sandblasted
Ti-8% In Alloy in Anhydrous
FNA (20% NO_2) at Ambient
Temperature

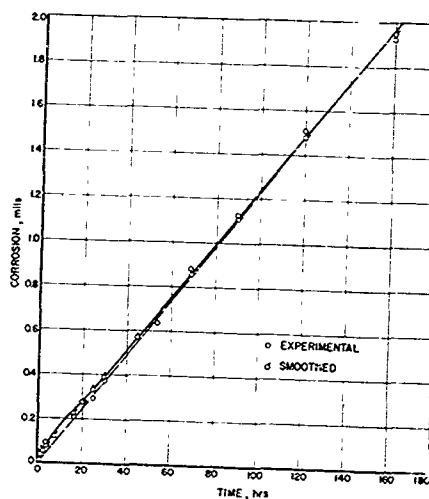


Figure 2. Corrosion of Vacuum-Stress-Relieved and Sand-
blasted Ti-8% Nb Alloy in Anhydrous FNA (20% NO_2)
at Ambient Temperature

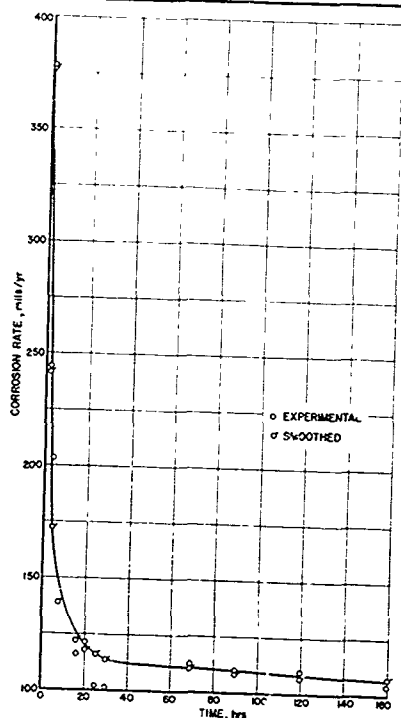


Figure 3. Average Corrosion Rates of Vacuum-Stress-Relieved and Sandblasted Ti-8% Mn Alloy in Anhydrous FNA (20% NO_2) at Ambient Temperature

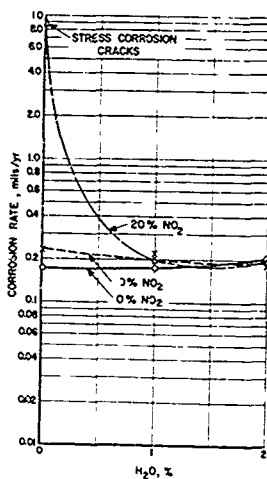


Figure 4. Average Corrosion Rates of Sandblasted Commercially Pure Titanium A55 in FNA at 30°C for 1 Week

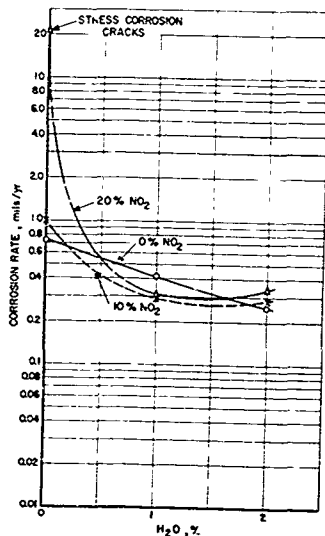


Figure 5. Average Corrosion Rates of Sand-blasted Commercially Pure Titanium Ti 100A in FNA at 30°C for 1 Week

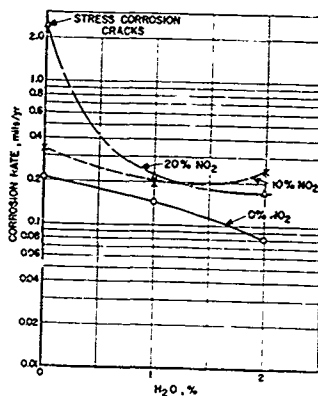


Figure 6. Average Corrosion Rates of Sand-blasted Titanium Alloy Ti 140A in FNA at 30°C for 1 Week

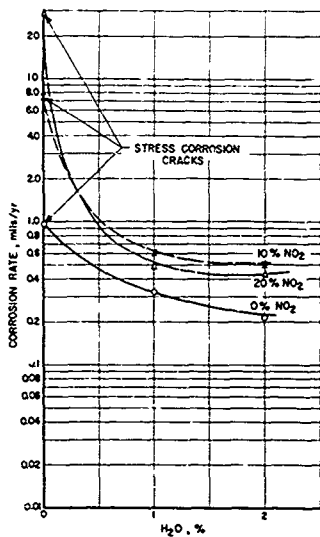


Figure 7. Average Corrosion Rates of Sand-blasted Titanium-6% Aluminum-4% Vanadium Alloy in FNA at 30°C for 1 Week

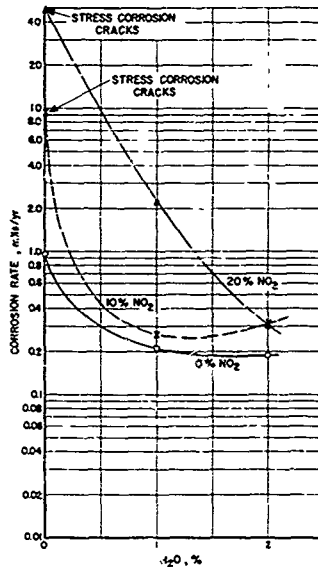


Figure 8. Average Corrosion Rates of Sand-blasted Titanium Alloy A110 AT in FNA at 30°C for 1 Week



Figure 9 Sheared Edge of Titanium-6% Aluminum-4% Vanadium Alloy after Storage for 1 Week at 30°C in Anhydrous FNA (20% NO_2) (Approx. 20X)



Figure 10 Photomicrograph of Edge of Sample of Fig. 9 (150X)

REFERENCES

1. Bomberger, H. B., "Titanium," *Industrial and Engineering Chemistry*, 47 (No. 9):2041, 1955.
2. Kiefer, G. I. and Harple, W. W., "Stress Corrosion Cracking of Commercially Pure Titanium," *Metals Progress*, 63(No. 2) 74-76, 1953.
3. Evers, U. R., *Metallic Corrosion Passivation and Protection*. London: Edward Arnold and Co., 1948.
4. Rittenhouse, J. B., Vango, S. P., and Whittick, J. S., *Corrosion and Ignition of Titanium Alloys in Fuming Nitric Acid. III. Study of Additional Chemical Factors*, Progress Report No. 26-3. Pasadena: Jet Propulsion Laboratory, January 30, 1956.
5. Rittenhouse, J. B., Vango, S. P., and Whittick, J. S., *Corrosion and Ignition of Titanium Alloys in Fuming Nitric Acid. II. Study of Additional Chemical and Metallurgical Factors*, Progress Report No. 26-2. Pasadena: Jet Propulsion Laboratory, November 30, 1955.
6. Hildebrandt, F., "The Demand for Uniform Testing in Corrosion Testing of Materials for the Construction of Chemical Apparatus," *Chemiker Zeitung*, 56:689-690, 1932.
7. Banks, R. R., and De Cecco, N. A., *Brazing and Soldering of Titanium and Its Alloys*, Report No. WAL 401/96-5. Chicago: Armour Research Foundation of Illinois Institute of Technology, 1953.

INITIAL DISTRIBUTION

Contract AF 33(616)-3066

1. Naval Ordnance Test Station
China Lake, California
Attn: Mr. R. W. Sprague
2. U. S. Naval Air Rocket Test Station
Lake Denmark
Dover, New Jersey
Attn: Mr. Terlizzo, Propellant Division
3. Aero et General Corporation
6352 North Irwindale Ave.
Azusa, California
Attn: Mr. C. Ross
4. Boeing Aircraft Corporation
Box 3107
Seattle 14, Washington
Attn: Mr. R. H. Nelson, Project Engineer
MX-1559
5. Boeing Aircraft Corporation
Box 3107
Seattle 14, Washington
Attn: Process Group
6. Bell Aircraft Corporation
Niagara Falls, New York
Attn: Mr. H. A. Campbell
7. United States Dept. of Interior
Bureau of Mines
Washington 25, D. C.
Attn: Mr. T. H. Miller, Acting Director
8. Rem-Cor Titanium Inc.
Midland, Pa.
Attn: Mr. W. L. Finley
9. Republic Steel Corp.
Massillon, Ohio
Attn: Mr. V. Whitmore
10. Titanium Metal Corp.
Henderson, Nevada
Attn: Mr. S. A. Herres
11. Mallory Sharon Titanium Corp.
Niles, Ohio
Attn: Mr. Lee Busch
12. North American Aviation Inc.
12214 Lakewood Blvd.
Downey, California
Attn: Mr. J. G. Berter, Director
13. Reaction Motors, Inc.
Rockaway, New Jersey
Attn: Mr. W. P. Munger, Chief Engr
14. Battelle Memorial Institute
505 King Ave.
Columbus, Ohio
Attn: Mr. C. B. Voldrich
15. Battelle Memorial Institute
505 King Ave.
Columbus, Ohio
Attn: Liquid Propellant Handbook Group
16. Commanding General
Redstone Arsenal
Huntsville, Alabama
Attn: Technical Library
17. Allegheny Ludlum Corp.
Watervliet, New York
Attn: W. Dykstra
- 18-35. Commander
Wright Air Development Center
Air Research and Development Command
Wright-Patterson Air Force Base, Ohio
Attn: WCR TH-3