SAND-74-0145
Unlimited Release

3151

THE REACTION OF URANIUM AND ITS ALLOYS WITH WATER VAPOR AT LOW TEMPERATURES

N. J. Magnani

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87123
and Livermore, California 94550 for the United States Atomic Energy
Commission under Contract AT (28-1)-789

Printed August 1974

Sandia Laboratories

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Issued by Sandia Laboratories, operated for the United States Atomic Energy Commission by Sandia Corporation.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SF 1004-DF(2-74)

SAND-74-0145

THE REACTION OF URANIUM AND ITS ALLOYS WITH
WATER VAPOR AT LOW TEMPERATURES*

N. J. Magnani
Physical Metallurgy Division

ABSTRACT

The rate of hydrogen generation of several uranium alloys exposed to 100% R.H. O_2 and N_2 at $75^\circ C$ were determined. The data show that as the level of alloy addition increases the rate of generation decreases and that O_2 inhibits the rate of generation. Mechanical properties tests have shown that at strain rates of 0.03 min^{-1} U-4.5 wt.% Nb aged at $260^\circ C$ for 80 hours is not affected by up to 6 month exposures to humidity while U-0.75 wt.% Ti aged $380^\circ C$ for 6 hours does show a significant decrease in ductility after 2 weeks exposure to moisture.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This document is
PUBLICLY RELEASABLE

Barnes
Authorizing Official

Date: 7-25-67

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGEMENT

The author would like to thank P. L. Watterberg for conducting the corrosion and mechanical properties tests and R. M. Merrill for the analysis of the hydrogen in the alloys.

TABLE OF CONTENTS

	<u>Page</u>
Acknowledgment.....	2
Introduction	5
Experimental Procedure.....	7
Results.....	9
Discussion.....	23
Summary.....	27
References.....	28

LIST OF TABLES

Table

I. Uranium Alloys.....	8
II. The Rate of Hydrogen Generation from Selected Uranium Alloys in 100% R.H. O ₂ and N ₂ at 75°C.....	13
III. The Mechanical Properties of U-4½ wt.% Nb and U-0.75 wt.% Ti Sheet Tensile Specimens (0.040" thick) after Exposure to Environment at 75°C.....	24

LIST OF FIGURES

Figure

1. The Rate of Hydrogen Generation of Selected Uranium Alloys Exposed to 100% R.H. O ₂ at 75°C. The alloy labeling is by wt.% addition. (U-4.5 wt.% Nb and U-7.5 wt.% Nb - 2.5 wt.% Zr data from <u>Ref. 6.</u>)	10
2. The Rate of Hydrogen Generation of Selected Uranium Alloys Exposed to 100% R.H. N ₂ at 75°C. The alloy labeling is by wt.% addition. (U-4.5 wt.% Nb and U-7.5 wt.% Nb - 2.5 wt.% Zr data from <u>Ref. 6.</u>)	11
3. U-0.75 wt.% Ti Exposed to 100% R.H. N ₂ at 75°C for 35 days.	17
4. U-0.75 wt.% Ti Exposed to 100% R.H. O ₂ at 75°C for 35 days.	17
5. U-2 wt.% Mo Exposed to 100% R.H. N ₂ at 75°C for 35 days.	19
6. U-2.25 wt.% Nb Exposed to 100% R.H. N ₂ at 75°C for 35 days.	19
7. U-6 wt.% Nb Exposed to 100% R.H. N ₂ at 75°C for 35 days.	21
8. U-6 wt.% Nb Exposed to 100% R.H. O ₂ at 75°C for 35 days.	21

Introduction

As is the case with numerous active metals, uranium reacts with water vapor to form an oxide and liberate hydrogen. The reactions that can occur are:¹

The solid reaction product has been identified as $\text{UO}_{2.0} - \text{UO}_{2.1}$ with 2-9% UH_3 depending on the relative humidity during the test.² Therefore the bulk of the hydrogen liberated by the reaction goes into the gas phase. A uranium specimen was completely oxidized at 80°C in a $\text{H}_2\text{O}/\text{D}_2$ mixture and the fixed hydrogen in the metal contained less than 1% D_2 indicating the UH_3 is formed during the metal- H_2O reaction step and not at a later time by gaseous hydrogen.² The authors proposed a mechanism for the oxidation involving OH^- as the diffusing species:

With the overall reaction at the uranium-uranium oxide interface being:

The $\text{H}^\cdot$ can then react with uranium to form UH_3 or combine to form H_2 gas. There is disagreement as to whether or not H_2 in the gas phase will increase the reaction rate with H_2O . It has been reported that wet H_2 reacts faster than wet

N_2 ,¹ but also reported that pressures of H_2 up to 6 atmospheres had no effect on the reaction rate.²

When O_2 is added to the uranium-water system the reaction rate is substantially reduced.^{1,3,4} Reductions in the uranium-water reaction rate of up to two orders of magnitude have been reported with concentrations of O_2 as low as 0.06 volume percent in moist flowing N_2 .¹ In a closed system once the O_2 is consumed the reaction rate resumes the rate observed in H_2O .³ It has also been reported that at relative humidities below 90%, hydrogen is not evolved in the presence of O_2 .³ Isotope studies have shown that the oxygen reacts with the liberated H_2 to reform water and that H_2O is still the oxidizing agent in H_2O/O_2 mixtures.³ In the water saturated conditions containing O_2 the oxide formed is $UO_3 \cdot 0.8H_2O$.⁴

Several mechanisms of O_2 inhibition of the uranium-water reaction have been proposed. Waber⁵ attributed the inhibition to differential aeration effects stifling the anodic reaction in oxygen rich areas. Kondo et. al.¹ proposed that O_2 reacts with the H_2 to reduce the H_2 available for UH_3 formation slowing the overall reaction rate since the UH_3 was a transitory intermediate phase in their mechanism. Baker et. al.³ proposed that a chemisorbed layer of O_2 on the oxide surface prevents the direct adsorption of H_2O and that a less fissured oxide is formed when O_2 is present, both of which could slow the reaction.

Compared to uranium there is very little information available on low temperature uranium alloy reactions with water vapor. Magnani and Romero⁶ studied U-4.5 wt.% Nb and U-7.5 wt.% Nb-2.5 wt.% Zr while Orman⁷ has investigated U-4.5 wt.% Nb, U-6 wt.% Nb, U-8.5 wt.% Nb, U-0.75 wt.% Ti and U-2.25 wt.% Nb. In the first investigation⁶ O_2 was found to inhibit the rate of hydrogen generation for both U-4.5 wt.% Nb and U-7.5 wt.% Nb-2.5 wt.% Zr

exposed to water saturated conditions at 75°C. The ternary alloy was also tested in wet N₂ which contained 2 and 9% H₂. No increase in generation rate over that in wet N₂ was observed. Orman⁷ found that most of the hydrogen generated by the reaction of U-4.5 wt.% Nb, U-6 wt.% Nb and U-8.5 wt.% Nb with water vapor at 125°C was adsorbed by the metal. He also found at 60°C that the bulk of the hydrogen from the reaction of U-0.75 wt.% Ti and U-2.25 wt.% Nb with water vapor was released as free H₂. Gravimetric studies conducted on the U-Ti alloy confirmed that the bulk of the hydrogen was liberated as free H₂.

This investigation was undertaken to obtain additional data on the rate of hydrogen generation from uranium alloy-water vapor reactions. Because of the deleterious nature of hydrogen there is considerable interest in preventing or at least minimizing its generation. In addition to obtaining the generation rates it was hoped that the hydrogen generation rates could be related to the level of alloy additions to the uranium and to the general corrosion rates. A correlation between hydrogen generation and general corrosion might then lead to a simple corrosion test for rating uranium alloys.

Experimental Procedure

The alloys tested in this investigation are shown in Table I. Several of the alloys were quenched from the γ (bcc) region with the γ phase being retained in the 6 and 8 wt.% Nb and the 10 wt.% Mo alloys. All other alloys transformed on cooling to various metastable structures. Corrosion specimens 1.3×10^{-3} m thick were sealed in glass vials together with a glass ampule containing ~1 ml of degassed water and either research grade N₂ or O₂. The ampules were broken and the vials placed in a 75°C oven for the duration of

TABLE I

Uranium Alloys

<u>Nominal Alloy Composition</u>	<u>Heat Treatment</u>
Uranium	Quenched
U-0.5 wt.% Ti	Quenched from the γ region
U-0.75 wt.% Ti	Quenched from the γ region
U-0.75 wt.% Ti	Quenched and aged at 380°C for 6 hours
U-2 wt.% Mo	Quenched from the γ region
U-2.25 wt.% Nb	Quenched from the γ region
U-6 wt.% Nb	Quenched from the γ region
U-8 wt.% Nb	Quenched from the γ region
U-10 wt.% Mo	Quenched from the γ region
U- $\frac{1}{2}$ Quad*(0.5 wt.% Nb,Zr,Mo,Ti)	As extruded
U- $\frac{3}{4}$ Quad*(0.75 wt.% Nb,Zr,Mo,0.5 wt.% Ti)	As extruded
U-1 Quad*(1 wt.% Nb,Zr,Mo,0.5 wt.% Ti)	As extruded
U-1 Quint*(1 wt.% Nb,Zr,Mo,0.5 wt.% Ti,V)	As extruded

* Alloys furnished by the Army Materials and Mechanics Research Center.

the test, which ranged from 7 days to 505 days depending on the reactivity of the specimens. After removal from the oven the gases in the vial were analyzed with a residual gas analyzer and pieces of the specimens were analyzed for residual H_2 . Contamination problems occurred in some of the wet N_2 tests where traces of O_2 were detected and these data were discarded.

The mechanical properties tests were conducted on sheet tensile specimens of U-4 $\frac{1}{2}$ wt.% Nb and U-0.75 wt.% Ti that were 1.0×10^{-3} m thick. The specimens were exposed to the environment in the same manner as the corrosion specimens. The 65 day and 148 day U-4 $\frac{1}{2}$ wt.% Nb tests were conducted a significant time after analysis of the gas phase while the rest of the tests were conducted 2 hours after the vials were opened, to allow the specimens to dry, and the gases were not analyzed. The mechanical properties tests were conducted in 45% R.H. ambient air.

Results

The results of the hydrogen generation rate experiments in wet O_2 are shown in Figure 1. The data represent the average of triplicate tests and are plotted versus atomic percent since the percent of the atoms that are uranium should be more important to the corrosion rate than the weight of the alloy additions. The labeling of the data in the figure is the more conventional wt.% notation. The data show a trend exists wherein the rate of hydrogen generation decreases as the uranium content decreases irrespective of the alloying elements. Three alloys are somewhat less reactive than might have been expected. U-0.5 wt.% Ti, U-4.5 wt.% Nb and U-7.5 wt.% Nb - 2.5 wt.% Zr.

The results of the tests conducted in wet N_2 are shown in Figure 2. Once again the data represent the averages of three tests except for 0.75

Figure 1. The Rate of Hydrogen Generation of Selected Uranium Alloys Exposed to 100% R.H. O₂ at 75°C. The alloy labeling is by wt.% addition. (U-4.5 wt.% Nb and U-7.5 wt.% Nb - 2.5 wt. % Zr data from Ref. 6.)

Figure 2. The Rate of Hydrogen Generation of Selected Uranium Alloys Exposed to 100% R.H. N₂ at 75°C. The alloy labeling is by wt.% addition. (U-4.5 wt.% Nb and U-7.5 wt.% Nb - 2.5 wt.% Zr data from Ref. 6.)

wt.% Ti, 1 Quint and 10 wt.% Mo which represent two tests and 1 Quad represented by 1 test. There is significantly more scatter in the trend of decreasing hydrogen evolution with percent alloy addition than observed in wet O_2 . The line drawn in Figure 2 is parallel to the line in Figure 1 but displaced upwards about 4X. The 2 wt.% Mo alloy generated hydrogen faster than uranium while anomalously no hydrogen was detected from U-6 wt.% Nb tests for times up to 320 days. The data represented in Figures 1 and 2 are also shown in Table II.

Prior to the start of the experiments a few tests were conducted to obtain an estimate of the H_2 evolution rate and O_2 consumption rate to allow for the proper selection of test times for the experiments. Figures 3 through 8 show several of the specimens after 35 days in test. Figures 3 and 4 show U-0.75 wt.% Ti specimens exposed to wet N_2 and wet O_2 respectively. The corrosion product in the wet N_2 test is UO_{2+x} while that in the wet O_2 test is thought to be $UO_3 \cdot 0.8H_2O$.⁴ Figure 5 shows a U-2 wt.% Mo specimen after exposure to wet N_2 . The vial contained 5000 torr of H_2 at the end of the test which lead to the formation of a great deal of hydride and disintegration of the specimens. The 2.25 wt.% Nb alloy in the same environment, wet N_2 , is shown in Figure 6. The specimen did not show very much evidence of corrosion compared to the U-0.75 wt.% Ti and U-2 wt.% Mo. Figures 7 and 8 show U-6 wt.% Nb specimens tested in wet N_2 and wet O_2 environments. There is no evidence of corrosive attack in the wet N_2 while there was in the wet O_2 . This was the only system where the reaction in wet N_2 occurred slower than in wet O_2 .

The H_2 content of all of the metals were determined after the tests. Only a small amount of the liberated hydrogen was absorbed by the metal in

TABLE II

The Rate of Hydrogen Generation from Selected Uranium Alloys in 100% R.H. O_2 and N_2 at $75^\circ C$

<u>Alloy</u>	<u>Environment</u>	<u>Time in Test (days)</u>	<u>% H_2 in the* System</u>	<u>Rate of Generation moles/m^2-day</u>
Uranium	Wet O_2	7	10	2.0×10^{-2}
Uranium	Wet O_2	15	49	5.4×10^{-2}
Uranium	Wet O_2	15	49	3.5×10^{-2}
Uranium	Wet N_2	7	50	1.7×10^{-1}
Uranium	Wet N_2	12	77	1.7×10^{-1}
Uranium	Wet N_2	12	70	1.6×10^{-1}
U-0.5 wt.% Ti	Wet O_2	7	0.3	8.4×10^{-4}
U-0.5 wt.% Ti	Wet O_2	38	7.9	6.2×10^{-3}
U-0.5 wt.% Ti	Wet O_2	88	2.5	9.0×10^{-4}
U-0.5 wt.% Ti	Wet N_2	7	31	9.8×10^{-2}
U-0.5 wt.% Ti	Wet N_2	12	66	1.4×10^{-1}
U-0.5 wt.% Ti	Wet N_2	28	72	6.8×10^{-2}
U-0.75 wt.% Ti	Wet O_2	7	4.0	9.5×10^{-3}
U-0.75 wt.% Ti	Wet O_2	14	9.7	1.0×10^{-2}
U-0.75 wt.% Ti	Wet O_2	21	9.5	6.8×10^{-3}
U-0.75 wt.% Ti	Wet N_2	12	61	1.1×10^{-1}
U-0.75 wt.% Ti	Wet N_2	21	71	8.7×10^{-2}
U-0.75 wt.% Ti ($380^\circ C/6$ hrs)	Wet O_2	7	1.6	2.9×10^{-2}
"	Wet O_2	7	1.8	4.5×10^{-3}
"	Wet O_2	14	13	1.2×10^{-2}
"	Wet N_2	7	7.7	2.2×10^{-2}
"	Wet N_2	7	22	7.1×10^{-2}
"	Wet N_2	21	54	6.5×10^{-2}
U-2 wt.% Mo	Wet O_2	7	0.2	4.2×10^{-4}
U-2 wt.% Mo	Wet O_2	38	7.9	6.0×10^{-3}
U-2 wt.% Mo	Wet O_2	88	1.7	4.5×10^{-4}

TABLE II (cont.)

<u>Alloy</u>	<u>Environment</u>	<u>Time in Test (days)</u>	<u>% H₂ in the* System</u>	<u>Rate of Generation moles/m²-day</u>
U-2 wt.% Mo	Wet N ₂	7	45	1.5×10^{-1}
U-2 wt.% Mo	Wet N ₂	7	73	2.8×10^{-1}
U-2 wt.% Mo	Wet N ₂	7	71	2.8×10^{-1}
U-2.25 wt.% Nb	Wet O ₂	14	1.8	2.3×10^{-3}
U-2.25 wt.% Nb	Wet O ₂	29	1.7	1.1×10^{-3}
U-2.25 wt.% Nb	Wet N ₂	14	25	3.9×10^{-2}
U-2.25 wt.% Nb	Wet N ₂	21	22	2.3×10^{-2}
U-2.25 wt.% Nb	Wet N ₂	21	19	1.8×10^{-2}
U-6 wt.% Nb	Wet O ₂	68	Not detected	$<1.2 \times 10^{-5}$
U-6 wt.% Nb	Wet O ₂	239	2.4	1.8×10^{-4}
U-6 wt.% Nb	Wet O ₂	320	1.8	1.1×10^{-4}
U-6 wt.% Nb	Wet O ₂	505	4.8	4.2×10^{-4}
U-6 wt.% Nb	Wet N ₂	68	Not detected	$<1.4 \times 10^{-5}$
U-6 wt.% Nb	Wet N ₂	239	Not detected	$<4.0 \times 10^{-6}$
U-6 wt.% Nb	Wet N ₂	320	Not detected	$<2.8 \times 10^{-6}$
U-8 wt.% Nb	Wet O ₂	70	1.5	3.7×10^{-4}
U-8 wt.% Nb	Wet O ₂	155	0.2	2.3×10^{-5}
U-8 wt.% Nb	Wet O ₂	320	0.2	7.9×10^{-6}
U-10 wt.% Mo	Wet O ₂	84	0.1	2.5×10^{-5}
U-10 wt.% Mo	Wet O ₂	180	0.2	1.5×10^{-5}
U-10 wt.% Mo	Wet O ₂	238	0.3	2.5×10^{-5}
U-10 wt.% Mo	Wet N ₂	70	0.5	1.4×10^{-4}
U-10 wt.% Mo	Wet N ₂	180	Not detected	4.8×10^{-6}
$\frac{1}{2}$ Quad	Wet O ₂	14	1.0	1.3×10^{-3}
$\frac{1}{2}$ Quad	Wet O ₂	29	3.8	2.5×10^{-3}
$\frac{1}{2}$ Quad	Wet O ₂	104	16.7	2.3×10^{-3}
$\frac{1}{2}$ Quad	Wet N ₂	14	4	7.3×10^{-2}
$\frac{1}{2}$ Quad	Wet N ₂	21	58	6.8×10^{-2}
$\frac{1}{2}$ Quad	Wet N ₂	21	50	4.3×10^{-2}

TABLE II (cont.)

<u>Alloy</u>	<u>Environment</u>	<u>Time in Test (days)</u>	<u>% H₂ in the* System</u>	<u>Rate of Generation moles/m²-day</u>
3/4 Quad	Wet O ₂	35	0.9	9.0×10^{-4}
3/4 Quad	Wet O ₂	86	9.7	3.6×10^{-3}
3/4 Quad	Wet O ₂	87	2.6	9.8×10^{-4}
3/4 Quad	Wet N ₂	70	2.7	1.3×10^{-3}
3/4 Quad	Wet N ₂	157	10.9	2.5×10^{-3}
1 Quad	Wet O ₂	35	5.1	4.7×10^{-3}
1 Quad	Wet O ₂	70	1.3	6.5×10^{-4}
1 Quad	Wet O ₂	157	6.1	1.3×10^{-3}
1 Quad	Wet N ₂	157	13	3.1×10^{-3}
1 Quint	Wet O ₂	35	0.2	1.5×10^{-4}
1 Quint	Wet O ₂	86	1.5	6.2×10^{-4}
1 Quint	Wet O ₂	157	2.7	5.6×10^{-4}
1 Quint	Wet N ₂	70	72	4.8×10^{-2}
1 Quint	Wet N ₂	72	56	3.7×10^{-2}

*There was a variation in the final pressures in the systems and therefore the % H₂ in the system is not linearly related to the moles generated.

Figure 3. U-0.75 Wt.% Ti Exposed to 100% R.H.
 N_2 at 75°C for 35 Days

Figure 4. U-0.75 Wt.% Ti Exposed to 100% R.H.
 O_2 at 75°C for 35 Days

Figure 5. U-2 Wt. % Mo Exposed to 100% R.H.
N₂ at 75°C for 35 Days

Figure 6. U-2.25 Wt. % Nb Exposed to 100% R.H.
N₂ at 75°C for 35 Days

Figure 7. U-6 Wt.% Nb Exposed to 100% R.H.
N₂ at 75°C for 35 Days

Figure 8. U-6 Wt.% Nb Exposed to 100% R.H.
O₂ at 75°C for 35 Days

the wet N_2 tests. The amount ranged from <1 to 8% with most specimens showing ~1% of the total liberated hydrogen adsorbed by the metal. In the wet O_2 environment significant quantities of hydrogen were detected in the metal. The amount in the metal ranged from 25 to 50% of the total liberated hydrogen. Only part of the increased percentage of H_2 in the metal is due to the fact less gaseous H_2 was generated in O_2 containing environments. The hydrogen analysis equipment had a LN_2 cold trap which prevented the water of hydration from the oxide from invalidating the hydrogen analysis. Therefore, more H_2 was either in solution in the metal or was UH_3 in either the metal or in the oxide. It is most likely that UH_3 is trapped in the oxide.

The results of the mechanical properties tests are shown in Table III. The data show that the yield and ultimate strengths were not significantly affected by the environment in either U-4.5 wt.% Nb or U-0.75 wt.% Ti. The ductility of the U-4.5 wt.% Nb was not affected by the environment. The elongations were >10% in all environments. The specimens broke out of the gage lengths in almost all of the tests leading to the lower limit of the ductility. Reductions of area in these specimens were also essentially the same, however, there was considerable scatter in the data. The U-0.75 wt.% Ti tests showed that the ductility was affected by the environment. The elongation was decreased by ~50% by exposure to water vapor, from 12.6% down to ~6%. The hydrogen pressure in the U-4.5 wt.% Nb tests was measured to be ~1 torr after 65 days and is estimated to be <10 torr for all of the mechanical specimen tests while the pressure in the U-Ti tests is estimated to be 450 torr in the N_2 tests and 150 torr in the O_2 tests.

Discussion

One of the difficulties encountered in uranium corrosion studies has been reproducibility from specimen to specimen. This study was no exception

TABLE III

The Mechanical Properties of U-4½ wt.% Nb and U-0.75 wt.% Ti Sheet
Tensile Specimens(0.040" thick) after Exposure to
Environment at 75°C[†]

Alloy	Environment	Time-in-test (days)	Yield Stress*		Ultimate Tensile* Strength		Percent* Elongation
			Ksi	MN/m ²	Ksi	MN/m ²	
U-4.5 wt.% Nb (245°C/24 Hr)	Vacuum	65	115	793	173	1190	>10%
	"	148	115	793	173	1190	>10%
	"	225	113	780	176	1210	>8.8%
	Wet O ₂	65	114	787	172	1190	>10%
		148	118	814	175	1210	>10%
		225	113	780	176	1210	>10.6%
	Wet N ₂	65	114	787	174	1200	>10%
		148	114	787	173	1190	>10%
		225	116	800	177	1220	>10.5%
U-0.75 wt.% Ti (380°C/6 Hrs)	Vacuum	14	137	945	216	1490	12.6
	Wet O ₂	14	146	1010	207	1430	6.7
	Wet N ₂	14	136	938	199	1370	5.1

[†]Tests performed at room temperature at a strain rate of .03 min⁻¹

*Averages of 2 tests for the U-4½ wt.% Nb and 3 tests for the U-0.75 wt.% Ti.

particularly with higher alloy additions. Another problem with low temperature uranium and uranium alloy corrosion is the large number of different types of tests that are being used which oftentimes give different orders of merit for the alloys. Because of these difficulties it is almost impossible to obtain a simple screening test accepted by the majority of investigators in the field. However, there is a great deal of interest in the amount of hydrogen generation from the metal-water reaction and since these data can not be necessarily inferred from other types of tests, it is felt tests directly measuring the rate of hydrogen generation are useful.

The data obtained in this investigation show that as the percent alloy addition increases the rate of generation of hydrogen decreases. It has also been shown that O_2 inhibits the generation of hydrogen in the saturated condition of the tests. If the relative humidity were reduced it is felt the inhibiting effect may even be greater since condensed water may be preventing ready access of O_2 to the surface. The U-6 wt.% Nb alloy is an exception to this trend in that no free hydrogen was detected in wet N_2 conditions, but small quantities were detected in wet O_2 tests. The data have also shown that in the metastable conditions tested, microstructure has no apparent effect on the corrosion rate. The alloys which retain the γ phase do react slower but only inasmuch as might be expected from the increase in alloy additions.

The data presented herein do not agree well with those of Orman obtained in 100% R.H. at $125^\circ C$.⁷ He found that with or without O_2 present the amount of hydrogen absorbed by U-4.5 wt.% Nb, U-6 wt.% Nb and U-8.5 wt.% Nb exceeded that generated as free hydrogen. In this investigation in the absence of O_2 only ~1% of the hydrogen was absorbed by the metal and in the presence of

O₂ the adsorbed hydrogen was always less than the free hydrogen. Tests conducted, at 60°C in 100% R.H. conditions in the absence of oxygen, by Orman⁷ on U-0.75 wt.% Ti and U-2.25 wt.% Nb yielded results that were similar to those obtained at 75°C in this investigation. However, he found small additions of O₂ completely suppressed the evolution of hydrogen which was clearly not the case in this investigation. These differences illustrate one of the problems in finding a well accepted screening test.

The mechanical properties data obtained at $\dot{\epsilon} = 0.03 \text{ min}^{-1}$ showed that U-4.5 wt.% Nb, which reacts with water vapor relatively slowly, is not affected by exposure to water vapor. Orman⁷ found for this alloy and U-6 wt.% Nb and U-8.5 wt.% Nb that the hardness increased during exposure to 125°C wet air. He also found that U-4.5 wt.% Nb and U-8.5 wt.% Nb showed some reduction of ductility while U-6 wt.% Nb was not significantly affected by tests of up to 40 days. Orman, states that the hardening could have been due to an aging response and not due to the environment, and since specimens were not exposed to the temperature in the absence of the environment a distinction between the mechanism cannot be made.

Jackson⁸ has reported that the ductility of U-0.75 wt.% Ti decreased as the relative humidity of the environment increased. In this investigation it was shown that the ductility of U-0.75 wt.% Ti decreased when the alloy was exposed to water vapor compared to a vacuum at 75°C. This occurred even though the mechanical test environment was the same for all of the tests, laboratory air with 45% R.H. The specimens were exposed to laboratory air for two hours to allow them to equilibrate prior to the mechanical tests.

It is felt that the reduction in ductility in both types of tests is due to the interaction of the alloy with the hydrogen released from the alloy-water reaction. It is important to note that in the severe test conditions used in

this investigation ($P_{\text{H}_2\text{O}} \approx 300$ torr) that exposure under stress (strain) is not required for degradation.

Summary

The rate of hydrogen generation from the uranium alloy-water vapor reaction at 75°C has been determined for a large number of alloys. The data have shown that as the alloy additions to uranium increase the rate of hydrogen generation decreases and that O_2 inhibits the generation rate. The U-2 wt.% Mo alloy generated hydrogen in the absence of O_2 faster than pure uranium while U-6 wt.% Nb in the same environment gave no evidence of hydrogen generation in test times of up to 320 days. The amount of hydrogen adsorbed by the alloys in wet N_2 environments was on the order of 1% of the total released hydrogen for all of the alloys. In the presence of O_2 between 25 and 50% of the total liberated hydrogen was found in the metal.

Mechanical properties tests on U-4.5 wt.% Nb and U-0.75 wt.% Ti have shown that the yield and ultimate tensile strength were not significantly affected by exposure to moisture at strain rates of 0.03 min^{-1} . The Nb alloy showed no affect of environment on ductility while the ductility of the Ti alloy was reduced 50% by exposure to moisture.

References

1. T. Kondo, E. D. Verink, F. H. Beck and M. G. Fontana, Corrosion, 1964, p. 314t.
2. M. McD. Baker, L. N. Less and S. Orman, Transactions of the Faraday Soc., 62, 1966, p. 2513.
3. M. McD. Baker, L. N. Less and S. Orman, Transactions of the Faraday Soc., 62, 1966, p. 2525.
4. S. Orman, Chemistry and Industry, 1963, p. 1692.
5. J. T. Waber, Proceedings of the Second United Nations International Conf. on the Peaceful Use of Atomic Energy, Geneva, Switzerland, 1958, p/699.
6. N. J. Magnani, H. Romero, Sandia Laboratories Report SC-RR-720635, 1972.
7. S. Orman, To Be Published, Physical Metallurgy of Uranium Alloys, Ed. J. J. Burke.
8. R. J. Jackson, Dow Chemical, Rocky Flats Division Report RFP-2048, 1974.

DISTRIBUTION:

Army Materials & Mechanics Research Center
Watertown, Mass. 02172

R. J. Rizzitano (1)
Charles Levy (1)
Milton Levy (1)

Los Alamos Scientific Laboratory
P. O. Box 1663

Los Alamos, N. M. 87544
B. Powell, CMB-6 (1)
D. J. Sandstrom, CMB-6 (1)
F. DuBois, WX-3 (1)

Richard Mah
Dow Chemical Co.
Rocky Flats Division
Box 888
Golden, Colo. 80401

J. W. Koger, 9201-3
Union Carbide Corporation
Y-12 Plant
Box Y
Oak Ridge, Tenn. 37830

A. Lopez
AFAFL/DLOU
Eglin AFB, Florida 32542

Capt. C. Simon
AFATL/DL/W
Eglin AFB, Florida 32542

L. C. Guynes - 1000 (2)
For: S. Anthony
C. Calow
Aldermaston, Berkshire, UK

A. Narath - 5000
Attn: Director - 5100
E. H. Beckner - 5200
A. Y. Pope - 5600
J. H. Scott - 5700

L. M. Berry - 5800
Attn: R. G. Kepler - 5810
R. L. Schwoebel - 5820
D. M. Schuster - 5840

M. J. Davis - 5830
N. J. Magnani - 5831 (10)
P. L. Watterberg - 5831
R. A. Sallach - 5831
R. W. Rohde - 5832
K. H. Eckelmeyer - 5832
J. L. Ledman - 5833
F. J. Zanner - 5833

D. M. Mattox - 5834
E. A. Aas - 8266 (2)
R. H. Meinken - 8310
L. J. Weirich - 8313
A. M. Torneby - 3141 (5)
Division 3151 (3)
For AEC/TIC (Unlimited Release)