1
ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

THE HIGH TEMPERATURE AQUEOUS CORROSION OF
URANIUM ALLOYS CONTAINING MINOR AMOUNTS OF
NIOBIUM AND ZIRCONIUM

by

J. E. Draley, S. Greenberg, and W. E. Ruther

April 1957

Metallurgy Division

Program 10.1.8

Portions of the material in this report have appeared
in the following Metallurgy Division Quarterly Reports:

ANL-5338 (pp. 91-94)	June 30, 1954
ANL-5382 (pp. 64-69)	September 30, 1954
ANL-5423 (pp. 72-76, 81, 82)	December 31, 1954
ANL-5439 (pp. 48-52)	March 31, 1955
ANL-5465 (pp. 62-64)	June 30, 1955
ANL-5489 (p. 31)	September 30, 1955
ANL-5541 (p. 20)	December 31, 1955
ANL-5623 (pp. 31-33)	June 30, 1956

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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.

2

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
INTRODUCTION	3
MATERIALS AND METHODS	4
RESULTS	8
I. Binary Niobium Alloys	8
II. Ternaries of Zirconium and Niobium	10
A. Selection of Composition	10
B. Heat Treatment	12
1. Necessity for Gamma Quench	12
2. Aging Characteristics	13
C. The Role of Hydrogen	21
D. Effect of Temperature	27
E. Galvanic Effect	28
F. Effect of Fabrication	28
III. Ternaries of Niobium and Tin	28
DISCUSSION	34
Aqueous Corrosion of Uranium	34
Alloying with Zirconium	36
The Role of Niobium	37
Damage by Hydrogen	38
Effect of Heat Treatment	39
Niobium-Tin Ternaries	40
ACKNOWLEDGMENT	41
APPENDIX	42
BIBLIOGRAPHY	44

THE HIGH TEMPERATURE AQUEOUS CORROSION OF URANIUM ALLOYS CONTAINING MINOR AMOUNTS OF NIOBIUM AND ZIRCONIUM

by

J. E. Draley, S. Greenberg, and W. E. Ruther

ABSTRACT

Alloys of uranium with niobium show good corrosion resistance in degassed, distilled water to about 315°C. The alloys must be quenched from the gamma phase in order to have high temperature corrosion resistance. The corrosion resistance is destroyed by over-aging at temperatures as low as 350°C. Of those tried, the alloy with best resistance to thermal aging is the uranium-5% zirconium-1-1/2% niobium alloy. At 290°C, optimum heat treatment can result in a rate of corrosion of about 6 mg/cm²/day. Certain moderate aging treatments, e.g., 400°C for two hours, result in improved corrosion resistance in the initial stages of corrosion. Alloys containing 3% niobium and small amounts of tin show promise. In addition to aging, the alloys are also sensitive to hydrogen content. Ultimate corrosion failure is believed due to absorption of corrosion product hydrogen.

INTRODUCTION

For those heterogeneous reactors in which hot water surrounds the fuel elements, it is highly desirable that the fuel material be compatible with the water. In this case perforation of the fuel element cladding would probably have only minor nuisance value, and a relatively low standard of cladding integrity could be used, resulting in fuel element costs substantially lower than those typical of present designs.

Uranium is not compatible with water in the sense used above. For this reason attempts have been and are being made to produce corrosion-resistant alloys. During the war this type of effort was made largely at the Metallurgical Laboratory and at MIT. This work has been reviewed by McWhirter and Draley,⁽¹⁾ and by Waber.⁽²⁾ Of the systems investigated, the most promising alloys (containing not more than several per cent of alloying elements) were binaries of uranium with niobium and ternaries containing niobium and zirconium.

4

More recently, and contemporary to the present investigation, considerable efforts have been expended at Westinghouse Atomic Power Division and at Battelle Memorial Institute with the same general objective. During these studies, more attention has been given to alloys containing somewhat more of the alloying constituents. In particular, the attractive corrosion-resistant properties of the quasi-stable gamma alloys has been studied intensively. Many of the results of these investigations have been reported by R. K. McGeary⁽³⁾ and by E. W. Cawthorne.⁽⁴⁾

The studies described here were largely supported as part of the program leading to the Experimental Boiling Water Reactor (EBWR), now in operation at Argonne. Major consideration was given to the requirement of maintaining the smallest feasible percentage of alloying constituents (minimum dilution), and an effort was made to achieve minimum parasitic absorption of neutrons by the additives.

Alloys first tried during this investigation were logically those which had shown aqueous corrosion resistance (at lower temperatures) in earlier work. Thus alloys containing a few per cent of niobium were tested first.⁽⁵⁾ As will appear later, it was logical and desirable to try other combinations leading to the development of a preferred alloy. These studies led to the development of the composition which was selected as the EBWR fuel (U-5% Zr-1-1/2% Nb).^{*} Subsequent to this development most of the effort in this program was devoted to studies of the behavior and properties of this alloy. As a result, the major fraction of this report deals with these studies. Attention is here restricted to the development and study of this alloy as a corrosion-resistant material. Production of the alloy and fabrication of fuel elements from it, the effects of heat treatment and the kinetics of transformation, and the effects of irradiation on both its corrosion behavior and its physical properties are described elsewhere. (6, 7, 8, 9, 10, 11, 12)

An additional part of this report is devoted to uranium-base niobium and niobium-tin alloys.

Further efforts are being aimed at providing an understanding of the mechanisms of uranium alloy corrosion and at producing new and better corrosion-resistant alloys.

MATERIALS AND METHODS

All alloys were vacuum melted and cast by the Foundry and Fabrication Group of the Metallurgy Division. Compositions of all those tested during this investigation are given in Table IIA (Appendix), together with the crucible material used. All were cast in a water-cooled copper mold, except for some of the latest ones which were prepared in heated graphite molds.

*All percentage compositions given in this report are by weight.

5

Samples were prepared and heat treated, as part of this investigation, by members of the Corrosion Research Group (the authors). In general, heat treatment consisted of quenching from the gamma phase, followed in some cases by aging at a relatively low temperature.

Most samples were gamma quenched from 1000°C in vacuum. The bare samples were suspended in a tantalum basket placed inside a resistance-heated, stainless steel furnace tube. Samples were maintained at 1000°C for one hour and then quenched by dropping into molten Woods Metal at 125°C, which was stored in a container at the bottom of the furnace tube. The system was pumped continuously during this cycle.

Some samples were heated to the gamma phase (maximum temperature 850°C) in liquid metal or salt and quenched in water or another medium to determine the effect of heat-treatment variables. The type of heat treatment (both quenching and aging) is indicated in the presentation of the results.

Because of the wide variation in times and temperatures of aging, three methods of aging were used:

- 1) sample in an evacuated ampoule placed in electric oven (low temperatures - long times);
- 2) sample placed in Vycor tube furnace with flowing argon or helium (low and medium temperatures - short and medium times); and
- 3) liquid metal (high temperature - short time).

Samples were air cooled after aging. There were enough samples aged by two of these methods to indicate that the method used was not a significant variable.

Samples are described by the original casting number and the location (when known) with relation to the ingot, indicated as T (top), B (bottom), or C (center). Preparation of the material is described as c (as cast) or r (rolled). Thus L-170B-r indicates the bottom section of casting L-170 in the rolled condition. Compositions are given in weight per cent.

The high temperature corrosion tests were conducted in stainless steel autoclaves, placed in forced convection ovens. An autoclave is shown in Figure 1. In most tests, samples were insulated from electrical contact with the stainless steel holder by means of synthetic sapphire rods, as shown in Figure 2. Some corrosion tests performed in the Argonne Reactor Engineering Division are also reported here. In these tests the alloy samples were allowed free contact with the bodies of the stainless steel test autoclaves.

6

FIGURE 1

HIGH TEMPERATURE AUTOCLAVE

FIGURE 2

INSULATING SAMPLE HOLDER

7

Before the first period of test the samples were wet-ground to 400 grit metallurgical paper. Whenever the sample shape made this procedure impractical, it was electropolished in a perchloric-acetic acid bath. Results indicate that there was no significant difference in corrosion behavior caused by this difference in procedure. Sample surface areas were measured, after which the samples were degreased in methyl alcohol, washed in distilled water and weighed. After each test period each sample was cleaned of loose oxide with wet Kleenex, dried under vacuum, and weighed. Where long corrosion tests were run, the values of the approximate amount of metal corroded were plotted as a function of time, and the slopes of the curves so obtained are described as the "corrosion rate" (areas used in the computations were the original sample areas). In many cases less complete corrosion data were obtained. In these cases the usual procedure has been to calculate the average rate of weight change during each particular exposure. Since nearly all of the corrosion product formed fell off, or was removed prior to weighing, weight losses closely approximated actual metal corroded. Hence, these average rates of weight change are referred to as "average corrosion rates."

Distilled water was used as the corroding medium unless otherwise indicated. This water was double distilled, passing through a cation exchange resin between the two distillation steps. The resistivity of the water was equal to or greater than one megohm-cm at the tap. The autoclave was filled with this water, heated to boiling and the water discarded. The sample and its holder were then placed in the autoclave; water was then added and again heated to boiling. A water sample was then withdrawn and the autoclave sealed while the water was still boiling. The specific resistance of this water sample was measured as a check on water quality and cleanliness of the autoclave. The value was typically several hundred thousand ohm-cm. Fresh water was added in this way for each exposure so that during long tests the water was replaced each time the sample was examined.

Hydrogen analyses were performed in an apparatus in which the uranium alloy sample was heated into the gamma range (about 850°C). By means of two Toepler pumps the hydrogen was passed, through a palladium valve, into a calibrated volume where its pressure was measured. That the evolution of hydrogen in the gamma phase is complete has been demonstrated by corroborative analyses run by combustion. For analyses of samples after corrosion test, sometimes the corrosion product was removed by grinding the samples clean, and sometimes it was left on and simply dried by evacuation at room temperature. For a few cases where both procedures were used on similar samples, the results were the same, inferring that the drying procedure adequately removed moisture, so that errors from this source are unlikely.

RESULTS

When samples of this group of alloys show satisfactory corrosion behavior in water, they become dark brown, with a faint luster. They also usually form a light scattering of shallow pits which increase in depth as exposure increases. Unusual appearance is noted in the appropriate place.

I. BINARY NIOBIUM ALLOYS

Just as the early work indicated that optimum corrosion resistance (at 100° and 178°C) was obtained by quenching these alloys from the gamma phase, so it was here observed. Alloys containing 3 and 6% niobium were observed to show good corrosion resistance in short time tests at 300°C. At this temperature, all 3% alloys which were cooled more slowly from the gamma phase disintegrated in short tests.

The results of long time tests (performed by the Reactor Engineering Division) on these alloys are given in Figures 3 and 4. It is observed that both alloys show better corrosion resistance as quenched; the difference is much less striking for the 6% alloy than for the 3% alloy. Also note that the presence of oxygen dissolved in the water made very little difference in the corrosion behavior of the 6% alloy at 290°C.

FIGURE 3

CORROSION OF U-3% Nb IN DEGASSED, DISTILLED WATER.
ALLOY QUENCHED FROM 800°C⁽¹³⁾

FIGURE 4

CORROSION OF U-6% Nb IN DEGASSED, DISTILLED WATER⁽¹³⁾

Although the 3% niobium alloy was shown to possess a considerable degree of corrosion resistance in the gamma-quenched condition, this property was adversely affected by aging (at relatively low temperatures) subsequent to the gamma quench. Aging for three days at 350°C destroyed the corrosion resistance to water at 300°C. Increasing the quenching temperature from 800° to 1000°C somewhat increased the resistance to aging. It is believed that aging during exposure to water at temperatures of 300°-325°C was at least partially responsible for the relatively short corrosion life of the alloy at these temperatures (one to two weeks at 325°C).

The 6% alloy showed the same type of sensitivity to aging, but to a lesser degree. Aging at 350°C did not destroy the corrosion resistance of the alloy at 260°C, but the rate increased by a factor of two or three. Sample failure did occur at 325°C and 360°C after aging.

The uranium-3% niobium alloy was anodic to Zircaloy-2. At 300°C and a sample separation of 0.5 cm, a current of about 2 microamp/cm² was observed before the sample support failed after two days at temperature.

10

As will be seen in the discussion of the uranium-5% zirconium-1-1/2% niobium alloy, it is believed that hydrogen exerts a marked influence on the corrosion of these alloys. This belief is confirmed by the following experiment with the uranium-3% niobium alloy.

Three gamma-quenched samples were simultaneously exposed in degassed distilled water for 5-1/2 hours at 325°C. One sample insulated from the autoclave served as the standard control. A current of about 1 milliamp/cm² was passed between the other two samples, which served as anode and cathode, respectively. Although the time of exposure was too short to result in physical damage to any of the samples, the average rate of corrosion was increased by the cathodic current and decreased by anodic current, as shown in Table I. These results are in accordance with the proposal that the liberation of hydrogen at the metal surface increases the corrosion damage.

TABLE I

Effect of Hydrogen on Corrosion of
Uranium-3% Niobium Alloy at 325°C

Sample	Average Corrosion Rate, mcd
Control	25
Anode	22
Cathode	31

A similar conclusion seems justified by another experiment. After 28 hours as the cathode in a hydrogen discharge tube ($\sim 1\text{-}1/2$ mamp/cm², 1000-1500 v), a sample of the 3% niobium alloy split during a one-day corrosion test in distilled water at 300°C. Charging the sample with hydrogen increased its susceptibility to aqueous corrosion damage.

II. TERNARIES OF ZIRCONIUM AND NIOBIUM

A. Selection of Composition

Although large amounts of zirconium (greater than 40%) are required for aqueous corrosion resistance at 260°C,⁽¹⁴⁾ only about 5-6% is required to produce a corrosion-resistant alloy at 100°-150°C.^(15,16) However, even in the gamma-quenched condition, the latter alloy forms and maintains a protective film only when there is oxygen dissolved in the water.^(15,16)

These facts led to the investigation of ternary alloys containing zirconium and niobium. These alloys had initially been investigated as part of a program to replace niobium with zirconium, since the latter has more

desirable nuclear properties. Both elements induce sluggishness in phase transformations, though niobium is considerably more effective. An alloy containing 1-1/2% each of niobium and zirconium disintegrated in less than twenty-four hours in degassed water at 260°C. There was little improvement in oxygenated water.⁽⁵⁾ An alloy of 4% zirconium plus 2% niobium was comparable to the 3% niobium alloy in corrosion behavior and resistance to aging. However, an alloy of 5% zirconium plus 1-1/2% niobium showed no deleterious effects after 237 hours aging at 350°C. Thus, at these niobium contents, approximately 5% zirconium appears to be optimum (the minimum satisfactory amount).

A series of alloys was then made to determine the minimum amount of niobium necessary to produce corrosion resistance in a ternary alloy containing 5% zirconium. Different amounts of niobium were added to portions of a master alloy (~5% Zr). All samples were quenched in Woods Metal after one hour in vacuum at 1000°C. Corrosion results are shown in Table II.

TABLE II

Effect of Niobium Additions to Uranium-5% Zirconium Alloy

Alloy	Average Corrosion Rate (72 Hr in Water at 300°C), mcd
H288 (0.51% Nb + 4.90% Zr)	Disintegrated
H289 (1.06% Nb + 4.85% Zr)	Disintegrated
H290 (1.47% Nb + 4.81% Zr)	14
H311 (2% Nb + 4.80% Zr)	15

It is indicated that more than 1% niobium is required, but that small additions beyond 1.5% do not result in improved corrosion resistance. This composition was chosen as the reference alloy for the fuel for the Experimental Boiling Water Reactor, and a concentrated effort was applied to determining and understanding its corrosion behavior.

Relatively small amounts of silicon were observed to be harmful to the reference alloy. No accurate measure of the amount required was made, although a casting (H-272) which contained 30 ppm silicon as an impurity was normal in corrosion behavior, while the addition of 300 ppm silicon to a portion of it (H-277) caused gamma-quenched samples to disintegrate during three days exposure to water at 300°C.

12

B. Heat Treatment

1. Necessity for Gamma Quench

The uranium-zirconium-niobium system has been thoroughly studied and analyzed.^(9,10) The discussion here is limited to that necessary for an understanding of the relationship between heat treatment and corrosion resistance.

Between 677°C and the melting point the reference alloy (5 Zr + 1-1/2 Nb) consists of a single-phase (gamma) structure. A two-phase (beta plus gamma) region exists in the narrow temperature range of 666° to 677°C. Below 666°C, the structure depends on the heat treatment received by the material.

Isothermal quenching from the gamma to the beta-plus-gamma region (and holding there for, say, 24 hours) followed by rapid quenching to room temperature produces alpha plus a martensitic (distorted alpha) phase. This structure is not corrosion resistant.

If the above procedure is followed except that the temperature of the isothermal quench is reduced to about 660°C, the room temperature structure consists of normal alpha and retained (metastable) gamma. This structure also lacks corrosion resistance.

Rapid quenching from the gamma phase to temperatures close to room temperature produces the martensitic (distorted alpha) structure. This structure is corrosion resistant. It is not known if the alloying elements are present as a submicroscopic dispersion or are in supersaturated solution. However, a second phase has not been detected at 2000X. This treatment and resulting structure is necessary for high temperature corrosion resistance.

The rate of quench is very important. One typical method of heat treatment consists of holding the sample at 1000°C for one hour and then quenching in molten Woods Metal at 125°C. In one such operation the sample caught up in such a position that only about one-half was immersed in the Woods Metal. A subsequent three-day corrosion test at 300°C resulted in almost complete disintegration of that part of the sample which was not immersed.

Additional experiments confirmed the importance of quenching rate. A series of samples were heated in lead at 800°C and quenched in water, molten Woods Metal at about 150°C, oil, and liquid nitrogen. The first two groups of samples were satisfactory in water at 290°C. The latter two disintegrated in less than four days. Presumably the samples quenched in liquid nitrogen were surrounded by a vapor blanket which reduced the rate of cooling.

13

Corrosion-resistant material is produced by quenching from temperatures in the range 725° to 1000°C. The materials tested apparently were homogeneous at these temperatures, since corrosion behavior was independent of time at temperature during gamma treatment, in the range of a few minutes to 5.5 hours.

2. Aging Characteristics

The aging characteristics of the alloy are of importance from the point of view of particular uses. Of equal interest is the fact that a study of the aging process can lead to an understanding of the nature of the corrosion resistance and the mechanism of the loss of corrosion resistance.

Over-aging destroys the corrosion resistance of the alloy. Failure of the alloy can take place either by complete disintegration or by cracking or spalling into several pieces. The latter is apparently a stage in the former. If an apparently sound piece which has cracked off is subjected to a short additional exposure, further severe cracking or complete disintegration usually takes place. This statement refers to cracking into several relatively equivalent pieces and not to minor chipping from the bulk of a sample.

As an arbitrary measure of the aging resistance of the alloy it was decided that a sample was resistant to the given combination of time and temperature if it did not fail in either of the above ways in two weeks of testing in degassed, distilled water at 290°C.

In Figure 5, the area above the curve represents heat treatments which caused failure in less than two weeks. Combinations of time at temperature below the curve did not cause failure as it has been defined. This curve is based on castings H-317, H-416, H-419, and L-170 in the as-cast and rolled conditions. Samples were quenched from 1000°C (in vacuum) and aged in argon, helium, or molten lead.

The corrosion life and approximate corrosion rate for each condition shown in Figure 5 can be seen in Table III. Aging for times insufficient to cause "failure" reduced short-time corrosion rates, with the optimum close to two hours at 400°C. This effect is illustrated in Figure 6.

As the time of exposure was increased the corrosion rates of cast gamma quenched and gamma quenched and aged material became equal. In some cases the corrosion rate of gamma-quenched material decreased (Figure 7, curve 3), while in others the rate of the quenched and aged material increased, as shown in Figure 8. (These figures are also

14

FIGURE 5

EFFECT OF HEAT TREATMENT ON CORROSION LIFE
AT 290°C OF GAMMA QUENCHED U-5% Zr-1 $\frac{1}{2}$ % Nb ALLOYS

TABLE III

Effect of Aging on Corrosion Resistance at 290°C of
Uranium-5% Zirconium-1 1/2% Niobium Alloy
Quenched from 1000°C

Aging Temp., °C	Aging Time, hr	Corrosion Life, Days	Approximate Average Corrosion Rate, mcd (before failure)	Aging Temp., °C	Aging Time, hr	Corrosion Life, Days	Approximate Average Corrosion Rate, mcd (before failure)
290	312	>28	12	400	4	25-31	10
325	72	>14	15	400	72	< 1	-
350	72	>14	12	420	1	< 1	-
350	500	14-22	13	420	4	< 1	-
350	1000	>14	13	425	0.17	>16	8
350	4368	< 2.6	-	425	0.33	>15	7
375	10	14-19	12	425	0.50-1.0	< 4	-
375	24	10-14	13	440	0.08	>15	5
375	72	6-13	11	440	0.17	11-14	7
400	1	56-63	6	450	1	<1	-
400	2	>53	6	480	0.017	<3	-
400	3	66-75	6				

15

FIGURE 6

SHORT-TIME EFFECT OF AGING ON CORROSION RATE OF
U-5% Zr-1-1/2% Nb ALLOY AT 290°C

FIGURE 7

EFFECT OF HEAT TREATMENT AND FABRICATION ON CORROSION
RESISTANCE OF U-5% Zr-1-1/2% Nb ALLOYS

16

used to illustrate other ideas and will be referred to again in subsequent sections.) It also appears that aging at 400°C decreased the corrosion life of the few samples tested for sufficient times.

Rolled material, however, was benefited for relatively long periods by aging at 400°C, as shown in Figure 7 (curve 2).

To eliminate the possibility that aging occurred during test, cast samples of alloy H-317 were tested as quenched, as quenched and aged at 400°C for two hours, and as quenched and aged at 290°C for 312 hours. The results are summarized in Figure 8. All samples showed appreciable periods of approximately equal corrosion rates. The reason for the subsequently increased rate of the sample aged at 290°C is not known. There were no visible cracks and the sample appeared in good condition.

Attempts to explain the mechanism of aging and its effect on corrosion resistance are complicated by the fact that the relevant processes apparently take place on a submicroscopic scale. However, the mechanism postulated below is in agreement with the observable facts.

As indicated above, the properly quenched alloy is a "distorted" alpha phase alloy of martensitic structure. Moderate aging produces a "cellular" structure within the martensite. Severe "over-aging" causes precipitation and agglomeration at the grain boundaries. These conditions are illustrated in Figures 9, 10, and 11.

17

FIGURE 9

17171
CHROMIC
ACID ETCH

500 X
VHN - 382
(30 Kg)

L170B - CAST - GAMMA QUENCHED

18

FIGURE 10

17318
Ames Etch

500 X
VHN - 566
(30 Kg)

L170B - CAST - GAMMA QUENCHED AGED 400° C - 2 HR.

19

FIGURE 11

17149
Ames Etch

500 X
VHN - 563
(30 Kg)

L170B - CAST - GAMMA QUENCHED AGED 475⁰ C - 3 MIN.

20

Although the sample aged at 475°C for three minutes was not corrosion tested, its structure is undoubtedly similar to one heated at 480°C for one minute. The latter sample was completely disintegrated after 4 days at 290°C in degassed, distilled water.

Several comments should be made concerning Figures 9, 10 and 11. First, the dark lines are probably borides. This casting had an unusually high boron content, i.e., 15 ppm. The "over-aged" sample also had the "cellular" structure but it was impossible to show both the "cellular" structure and grain boundary effect with one etch. Neither the "cellular" structure nor the grain boundary precipitation could be shown to exist on the as quenched sample. The grain boundary effect was revealed only on the "over-aged" sample.

Although the above results are useful in explaining differences between extremes of heat treatment, it appears that conventional optical metallography can throw no light on more subtle differences. A group of gamma-quenched samples were aged at 425°C for periods ranging from 10 minutes to two hours, thus crossing the region from good to poor corrosion resistance. Metallographic examination revealed nothing definite, but there was a hint of grain boundary precipitation in the specimens aged longest.

X-ray diffraction results for the same group of samples (and for a few others) are much more interesting. In Table IV it is indicated that a significant drift in the 2θ value toward that of α uranium accompanies increased aging. This can be explained as the precipitation of a submicroscopic phase, followed by agglomeration of the precipitate. At the same time enough line sharpening was observed to indicate strain relief. It would thus appear that agglomeration of the precipitate and return of the lattice dimensions to those of α uranium are responsible for loss of corrosion resistance. The sample aged at 375°C was corrosion tested previous to X-ray analysis. Hydrogen pick-up and/or concurrent aging may have affected its 2θ value.

Included in the study of aging phenomena was an attempt to correlate corrosion resistance and hardness. No such correlation was found. It appears that hardness changes in this material occur as a consequence of more than one type of reaction. It is thus possible to produce samples having the same hardness, but showing wide variations in corrosion resistance; conversely, aging (within limits) gamma-quenched alloy increases its hardness considerably, but produces relatively little difference in corrosion behavior. This is illustrated by the hardness values in Table IV.

21

TABLE IV(16)

Effect of Aging on Lattice Parameters and
Corrosion Resistance of Uranium-5%
Zirconium-1 1/2% Niobium Alloy

Aging**		2 θ Angle for (111)	Corrosion Resistance at 290°C*	VHN 30 Kg
Temp., °C	Time			
as quenched		39.1	good	450
375***	72 hrs.	39.15	borderline	
425	10 min.	39.3	good	551
425	20 min.	39.3	good	564
425	40 min.	39.35	bad	547
425	2 hrs.	39.4	bad	604
425	4 hrs.	39.5	bad	600
440	5 min.	39.35	good	
475	3 min.	39.4	bad	
(α Uranium)		39.5	bad	

*good and bad indicate no failure and failure, in two weeks exposure to water, respectively.

**all alloys quenched from 1000°C.

***this sample had been corrosion tested previous to X-ray analysis (290°C-13.7 days).

C. The Role of Hydrogen

The standard heat-treatment procedure includes heating in a vacuum tube furnace at 1000°C. Considerable gas (believed to be largely hydrogen) is evolved in this process. In an effort to learn whether corrosion behavior is influenced by this gas, adjacent samples from the same rolled ingot were treated in vacuo and in molten lead.

The corrosion of these samples in water at 290°C is shown in Figure 12. The sample heat treated in helium was included to reproduce the thermal history of the vacuum-treated sample. It is inferred that the gas content of the metal, as received, is detrimental to its corrosion properties.

22

FIGURE 12

EFFECT OF GAS REMOVAL ON CORROSION AT
290°C OF U-1-1/2% Nb-5% Zr ALLOY

A similar result can be deduced from the corrosion of the sample quenched from salt (the eutectic of Li_2CO_3 and K_2CO_3), as shown in Figure 7, curve 5. For the first twelve days its corrosion rate was the same as the sample differing only by having the vacuum heat treatment. Subsequent to that time, however, the salt-treated sample continued to corrode at the same rate while the corrosion rate of the vacuum-treated sample decreased by 40%. The hydrogen content of this particular salt-treated sample was not determined; however, similar samples given the same treatment contained about 35 ppm hydrogen. Vacuum-treated metal contains little or no hydrogen.

It is thought that hydrogen is frequently responsible for poor corrosion resistance, and particularly for failure by cracking. A mechanism has been proposed, both at Argonne and Westinghouse Atomic Power Division, to account for the cracking phenomenon. First, hydrogen produced in the corrosion reaction diffuses into the metal. Accumulation of hydrogen in specific locations, either as molecular hydrogen or as uranium hydride, produces sufficient local stress to cause cracks. Such cracks may be at or near the surface or may be a series of cracks starting from the interior. The access of water to the metal in the cracks then produces oxide, of increased volume, and the crack is further propagated by this wedging action.

Hydrogen analyses of corroded samples show direct correlation with the amount of metal corroded. In Table V, such data have been treated to show the per cent of the hydrogen produced which was

23

absorbed in the alloy. After a short initial period the percentage of hydrogen absorbed remained constant for similar samples from the same piece.

TABLE V

Hydrogen Build-up as Function of Corrosion Time
(Alloy H-416C-c, gamma quenched, aged 2 hours at 400°C)*

Time (hours)	Metal Corroded (mg)	H ₂ in Corroded Sample (ppm)	% of Total H ₂ Produced that is Found in Sample
113	234	4.0	1.14
274	692	6.5	0.71
401 (Chip out of sample)	848	7.6	0.69
642 (Sample cracked into 3 pieces)	1127	13.9	0.71

*Four identical samples were tested for the times indicated.
Initial hydrogen content (after heat treatment) was 0.9 ppm.

When samples from different sources were corroded, there was not always the same fraction of the produced hydrogen absorbed into the metal. It is interesting to observe in Table VI, however, that the rate at which the hydrogen accumulated was approximately the same for all the samples, independent of their corrosion rates. The data from the second sample show that "loading" the material with hydrogen (by treatment in salt) before corrosion caused a higher corrosion rate. However, the absolute rate of hydrogen pickup by the sample (during corrosion) was not increased. As indicated above, an identical sample of the "loaded" material continued to corrode at the initial rate for at least 55 days, so that the shorter exposure time for the second sample in Table V does invalidate the argument.

Although the rate of hydrogen pickup was approximately the same, the corrosion-induced cracking was not. Assuming that this type of cracking is caused by corrosion product hydrogen, it must be supposed that high local hydrogen concentrations in the metal cause it, rather than the total amount present. The following experimental results support this hypothesis.

24

TABLE VI

Hydrogen Absorption in Corroding Alloy

Sample and Heat Treatment	Test Time at 290°C (days)	Average Corrosion Rate (mcd)	% of H ₂ Produced That Entered Metal	Rate of Hydrogen Build-up in Metal (μg/cm ² /day)	Condition After Test
<u>H-416C-c</u> Gamma quenched from vacuum, aged 400°C, 2 hours	26.7	8.6	0.7	1.09	Cracked
<u>L-170B-c</u> Gamma quenched from salt	18.9	9.4	0.6	0.95	No Cracks
<u>H-419B-r</u> Gamma quenched from vacuum, aged 400°C, 2 hours	48.9	6.7	0.96	1.07	Cracked
<u>L-170B-c</u> Gamma quenched from vacuum	47.9	6.5	0.97	1.06	No Cracks

A quenched and aged specimen contained 0.9 ppm hydrogen. After about eleven days of testing at 290°C the sample was cut in half and analyzed for hydrogen. The results were 5.7 and 8.1 ppm (± 0.1 ppm). It is significant that the piece with the higher hydrogen content had a subsurface crack which was revealed in sample preparation.

The salt-treated sample referred to in Table VI contained about 35 ppm hydrogen after heat treatment. Very likely this was uniformly distributed in the body-centered, cubic gamma uranium during the treatment. After an additional hydrogen build-up of 8 ppm during the corrosion test there was no evidence of cracking. Thus a total quantity of hydrogen which causes cracking in a sample in which it is not uniformly distributed did not cause cracking here. Perhaps the original (uniformly distributed) hydrogen enhanced the diffusion of the corrosion product hydrogen so that it too was uniformly distributed.

A group of samples which had been quenched from salt were aged in a helium atmosphere at 400°C for various periods of time and tested for 71 hours in degassed, distilled water at 290°C. The aging times bracketed that for optimum corrosion resistance of a vacuum-treated sample, i.e., approximately two hours. The results are shown in Table VII.

The as-quenched sample reacted typically. The behaviors of the aged samples were completely different from that of vacuum quenched and similarly aged metal, in that the corrosion resistance was destroyed.

25

It seems likely that during the aging process the hydrogen concentrated, perhaps at grain boundaries. These concentrations might act as nuclei for further local hydrogen buildup, especially if the hydrogen is present as hydride. The analytical samples consisted of small pieces of metal close to cracked surfaces. As expected, very high hydrogen contents were found.

TABLE VII

Effect of Aging on Corrosion Resistance and Hydrogen Absorption of Uranium-5% Zirconium-1 1/2% Niobium Alloy (L-170B - as cast - Quenched from Salt at 850°C)

Sample	Aging Time at 400°C (Hr)	Corr. Rate (mcd)	Hydrogen Content After 3 day Test (ppm)	Appearance of Sample after Test
1	0	13.5	60	Dull. Pitted
2	1	337*	832	Sample cracked into irregularly shaped piece and slurry. This piece in good condition.
3	2	450*	1220	Same as above.
4	3	616*	1340	Same as above.
5	4	-	-	Completely disintegrated.

*Based on remaining piece.

When the hydrogen content of the alloy becomes greater than its solubility, it has been expected that a (new) hydride phase will form. Efforts to observe such a phase in a number of samples of the sort previously discussed were unsuccessful. It was therefore attempted to obtain higher total hydrogen content as follows. A duplicate sample of L-170 B-c was quenched from salt at 850°C and aged in helium at 400°C for three hours. It was then exposed to degassed, distilled water at 290°C for twenty-four hours. At the end of this period the sample had a rough, heavily pitted, irregular surface; it had corroded at an average rate of 2126 mcd. The hydrogen content was 1100 ppm. The unexpectedly high corrosion rate (as compared with data in Table VII) could have been due to an inadequate quench. However, the object of obtaining a sample with high hydrogen content for metallographic study was achieved.

The sample was examined metallographically after heat treatment, after corrosion, and after hydrogen analysis.* The respective hydrogen contents were approximately 35, 1100, and 0 ppm. The photomicrographs appear in Figure 13. Only the sample with the high hydrogen content has

*The hydrogen analysis produces a slow cooled alloy and the resultant structure is very complex. The sample was therefore gamma quenched and aged after analysis in order to produce a structure more conducive to evaluation.

FIGURE 13

After Heat Treatment
250X - Ames
~35 ppm H₂ (17969)

After Corrosion
500 X - Ames
1150 ppm H₂ (18234)

After H₂ Analysis
500X - Ames
0 ppm H₂ (18308)

EFFECT OF HYDROGEN ON STRUCTURE OF U-5% Zr-1 $\frac{1}{2}$ % Nb ALLOY

27

what may be described as a "salt and pepper" effect. This structure has been found in this alloy only in samples containing high hydrogen contents. It is therefore inferred that the structure is hydride.

The difficulty of forming the (proposed) hydride is in line with the report that the addition of as little as 0.5% zirconium to 10.5 and 12% molybdenum alloys virtually eliminates the precipitation of hydride.⁽⁴⁾

It would be desirable to identify the new phase as the hydride in a more rigorous manner, for instance by X-ray or neutron diffraction. However, the highest hydrogen concentrations produced to date are below the threshold (2000 ppm or greater) of detection and identification by these methods. The particles are too small to be identified by standard micro-focus X-ray equipment.

Hydrogen can also be introduced into the sample by exposing it as the cathode in a hydrogen discharge tube. Such a sample (after 24-hour bombardment) was cracked after exposure to water and steam (because of autoclave leakage, part of the test involved a steam exposure) at 300°C for three days. A similarly tested, but non-bombarded, sample corroded in the normal manner.

D. Effect of Temperature

Water temperature affects both the corrosion rate and the useful life of this alloy. As indicated earlier, simultaneous aging may occur at sufficiently high temperatures. Figure 14 is representative of tests performed by the Reactor Engineering Division. The effects of temperature on corrosion rate and life are illustrated.

FIGURE 14

EFFECT OF TEMPERATURE ON CORROSION
BEHAVIOR OF GAMMA QUENCHED
U-5% Zr-1-1/2% Nb ALLOY

E. Galvanic Effect

As in the case of the uranium-3% niobium alloy, the uranium-5% zirconium-1 1/2% niobium alloy was anodic to Zircaloy-2. At 300°C and a sample separation of 0.5 cm, a current of about 2 microamp/cm² was observed.

F. Effect of Fabrication

The bulk of the data considered to this point have been for cast samples. The main difference in behavior between cast and rolled material is the long-time response of corrosion behavior to aging.

As noted in Section B, cast gamma-quenched samples approach the same corrosion rate after 10-14 days exposure, regardless of whether they are aged before testing. Aging also tends to reduce their corrosion lifetime.

In the case of rolled samples, moderate aging (2 hr at 400°C) appears to increase the corrosion life and decrease the corrosion rate (through the useful life of the material). This effect has been illustrated in Figure 7. In addition, a sample identical to the vacuum quenched and aged sample of Figure 12 (except that it was not aged) was tested under the same conditions. Before failure the corrosion rate was about 16 mcd; it failed in 9.7 days. In contrast, the aged sample had a rate of 10.1 mcd before failure at 31 days.

In addition to alloys prepared by conventional casting procedure, some material prepared by powder metallurgy techniques (Sylvania) was also tested. In general, corrosion rates were higher and corrosion life shorter, presumably because of porosity.

III. TERNARIES OF NIOBIUM AND TIN

Simultaneously with the development of the zirconium-niobium ternary alloy, an attempt was made to increase the thermal stability of the 3% niobium alloy.

Additions of (20% of the atom per cent of niobium) iron, nickel, silicon, and tin were made to the 3% niobium alloy. The iron alloy could not be rolled without cracking. Results of tests in 300°C degassed, distilled water on the other alloys as quenched, and quenched and aged, are shown in Table VIII.

It is evident that only the alloy containing tin is an improvement over the 3% niobium binary alloy.

29
TABLE VIII

Effect of Ternary Additions on Corrosion Resistance
of Uranium-3% Niobium Alloy

Alloy and Composition*	Average Rate After Quench from 800°C (mcd)**	Average Rate (Quenched, Then Aged 50 Hours at 350°C) (mcd)**
H273 3.5% Nb	7.4	Disintegrated
H279 3.6% Nb + 0.18% Si	342	Disintegrated
H281 3.5% Nb + 0.37% Ni	86	290
H282 3.5% Nb + 0.61% Sn	25†	19

*H279, 281 and 282 made by adding indicated amounts of Si, Ni, or Sn to H273.

**Approximately 90 hour test.

†Sample had slight crack after 72 hrs. Total test duration 161 hrs. At this time a piece had chipped out.

This alloy (as quenched from 1000°C) was then subjected to additional aging treatments. The results are tabulated in Table IX.

TABLE IX

Effect of Aging on Corrosion Resistance of Uranium-3.5%
Niobium-0.61% Tin Alloy (H-282)

Aging Treatment *	Corrosion Test (300°C)	
	Time of Test (hours)	Average Rate (mcd)
375°C - 24 hours	73** 139	17 Essentially Disintegrated
400°C - 24 hours†	72 205	14 14
425°C - 24 hours	72	185

*Specimens first quenched from 1000°C.

**Crack noted in specimen.

†This portion of the casting contained 0.71% Tin.

The above data indicate that the thermal aging resistance of 3% niobium-0.7% tin alloy may be superior to that of the 5% zirconium-1.5% niobium alloy.

The difficulty in obtaining homogeneous alloys and reproducible data are also indicated. This difficulty was encountered in the further study of the niobium-tin alloys. During this study all corrosion samples were cut from rolled alloys.

A series of 3% niobium alloys containing 0.25 to 1.60% tin were prepared. Results of short-time tests at 300°C appear in Table X. The alloys were tested, as quenched from 1000°C, in degassed, distilled water and in degassed, distilled water containing 50 ppm nickel ion (added as NiSO_4). Work on aluminum corrosion⁽¹⁷⁾ had indicated that the addition of nickel sulfate to the test water prevented penetration of the metal by corrosion product hydrogen (by the formation of nickel cathodes on the metal surface). As indicated previously, hydrogen penetration is believed responsible for failure of the uranium alloys by cracking.

TABLE X

Corrosion of Gamma-Quenched Uranium-3%
Niobium + Tin Alloys at 300°C

Alloy	Condition	Time (Hours)	Average Corrosion Rate for the test (mg/cm ² /day)	Comments
H356 3.12% Nb 0.26% Sn	Distilled	64	18.5	Etched appearance
	50 ppm Ni ⁺⁺	64	31.4	Etched appearance
H350 3.18% Nb 0.52% Sn	Distilled	66	39.5	Slight crack on one end
	50 ppm Ni ⁺⁺	66	29.9	Slightly lustrous
H352* 3.22% Nb 1.00% Sn	Distilled	40	44.7	Etched appearance
	50 ppm Ni ⁺⁺	40	38.8	Etched appearance
H354 3.24% Nb 1.63% Sn	Distilled	66	80.4	One end crumbling
	50 ppm Ni ⁺⁺	66	27.6	Grain structure apparent on both ends

Note: For purposes of comparison, 3% Nb alloys containing no tin have "corrosion rates" under the same conditions in degassed distilled water of between 7 and 14 mg/cm²/day.

*2300 ppm C

31

It is apparent that increasing the tin content increased corrosion rates during short exposure to distilled water, and that the presence of nickel ion in the water reduced the tendency to crack. The presence of nickel also produced a corrosion rate relatively independent of tin content (but considerably higher during the first 2-3 days exposure than that of the best tin alloy in distilled water).

The tests in distilled water were continued on alloys H356 and H352. In addition, alloy H357 (3.14% Nb + 0.78% Sn) was tested under the same conditions. All failed by cracking or crumbling in a total time of 11 days or less. Duplicate samples tested at approximately the same time at 290°C gave the same results.

The presence of nickel ion increased only slightly the corrosion life of these as-quenched alloys (except the 0.52% Sn alloy). Failure times were 16 days or less. The life of the 0.52% tin alloy was considerably increased: chipping was not observed until after 61 days. The corrosion behavior of this alloy is illustrated in Figure 15. After 61.3 days a section had chipped out of the sample.

After 67 days the sample was cut in half (through the defect) and photographed. Internal cracks, not visible in the original surface, are clearly revealed in Figure 16. This type of behavior is believed typical of the failure pattern of the alloys considered in this report.

32

FIGURE 16

Macro 16828

37X

INTERNAL CRACKS IN U-3.2% Nb-0.52% Sn
68 DAYS - 290°C - 50 PPM Ni⁺⁺

Another sample of the 0.52% tin alloy was platinized in a solution of chloroplatinic acid containing lead acetate. It was thought that the platinum might act in the same manner as the nickel. However, only minor improvement resulted. Chipping was noted after 7.5 days and the sample had started to split after 14.5 days. The effectiveness of the platinum plate is apparently only as good as its adherence. At the end of the test, no detectable platinum remained (microscopic and spectrographic examination).

Because of the erratic behavior of these alloys in water it was decided that additional data were necessary in order to permit realistic evaluation of the effect of nickel ion. Another sample of the 0.52% tin alloy was tested in the gamma-quenched (1000°C) condition in degassed, distilled water at 290°C. The test was discontinued after 37 days. Results are in Figure 15. There was no evidence of cracking or failure of any kind. This

33
 behavior was in sharp contrast to that of two samples of the same casting previously tested under the same conditions; these had failed by cracking or crumbling in 3.7 days or less.

This series of tests is indicative of the problems associated with the study of the niobium-tin alloys. The explanation is not readily apparent. There was no evidence of gross inhomogeneity. It is possible that the alloy may be brittle and subject to quench cracks. Such cracks were noted in many cases and the known affected samples were discarded. However, it is certainly possible that samples with internal or micro external cracks were tested.

The alloys were subjected to a variety of aging treatments after quenching from 800° or 1000°C. These treatments are listed in Table XI.

TABLE XI

Aging Treatments

Temp. °C	Time
250	6 hr
350	6 hr
370	24 hr
400	1 hr; 24 hr
425	5 min; 24 hr

Except for the instances noted below, all heat treatments resulted in failure by cracking and/or crumbling after exposures of 13.5 days or less at 290°C. The 3.1% niobium-0.26% tin alloy (quenched from 800°C and aged at 350°C for 6 hours) failed during the test interval 20-25 days. Samples of the 3.1% niobium-0.78% tin alloy were quenched from 800°C; some were aged at 250°, and some at 350°C. These had lives of greater than 72 days, and of about 40 days, respectively, at 290°C. The results for this alloy are summarized in Figure 17. Changing its aging temperature changed the corrosion lifetime, but apparently did not change the corrosion rate prior to failure.

Figure 18 shows the change in structure which accompanied aging a quenched alloy. The changes were similar to those taking place in 5% zirconium-1 1/2% niobium alloy, i.e., precipitation and agglomeration at the grain boundaries.

34

FIGURE 17

The niobium-tin alloys are perhaps potentially as corrosion resistant as any of the high uranium distorted alpha alloys discussed in this report. However, no definite conclusion can be made until reproducible data are obtained.

Niobium-tin alloys fabricated by powder metallurgy methods were also tested. As for the zirconium-niobium alloy prepared by this method, corrosion rates were higher than those for conventionally cast metal.

DISCUSSION

Aqueous Corrosion of Uranium

It is considered helpful to discuss some aspects of the mechanism of the aqueous corrosion of uranium and then to show how the situation is modified by alloying. The results of this investigation will be used to support the belief that hydrogen produced as a product of the corrosion reaction has a considerable influence on corrosion behavior.

As unalloyed uranium corrodes in air-saturated distilled water at room temperature it forms a thin continuous and protective film of uranium dioxide. Samples of the metal in this environment develop typical interference-color films, and the progress of corrosion can be estimated from the apparent film thickness. After sufficiently long exposure, however, points of local breakdown of this film are observed. At these points

35
FIGURE 18

Ames Etch
Quenched from Salt - 850°C

Ames Etch
Quenched-850°C and Aged-400°C-3 hrs.

EFFECT OF AGING ON U-3.1% Nb-0.25% Sn

the corrosion product is fine granular uranium dioxide. Where this type of product is formed, the rate of corrosion is considerably higher. With further exposure time these points of breakdown gradually spread, and it is inferred that eventually most of the surface would be corroding at the more rapid rate characteristic of the situation where the relatively unprotective corrosion product is formed.⁽¹⁾ It is considered, and the idea is developed in a publication by two of us,⁽¹⁸⁾ that these points of local breakdown represent places at which corrosion product hydrogen reacts beneath the protective film to form uranium hydride. This hydride then prevents bonding between the oxide film and the metal. Since this bonding appears to be a necessary requirement for the stability of thin oxide films of this type, the corrosion product takes its more stable form, a mass of fine crystals.

It is essential that there be some oxygen dissolved in the water in order to have the protective film. The means by which the oxygen acts cannot be stated unequivocally, but it appears reasonable to suppose that oxygen adsorbed on the protective oxide film will prevent the entry of hydrogen into the film, and will hence prevent access of hydrogen to the uranium surface. The fact that breakdown ultimately occurs indicates that the prevention of the entry of hydrogen into the oxide film is not complete. In the absence of dissolved oxygen, corrosion always proceeds on initially clean metal at the rate characteristic of the situation where there is no stable protective film.⁽¹⁾

As the temperature is increased it is perhaps more difficult to prevent the access of some of the hydrogen to the metal surface, and the solubility of oxygen in the water is reduced. Consequently there is a temperature above which the formation of the highly protective film is not observed on unalloyed uranium. In air-saturated water this temperature is about 60° to 70°C. The addition of hydrogen peroxide to the water apparently increases this temperature somewhat.⁽¹⁾

Alloying with Zirconium

By the addition of more than a minimum amount of zirconium the apparent sensitivity to the hydrogen effect can be considerably reduced, so that the protective film forms in boiling distilled water on a uranium-5% zirconium alloy.^(15,16) The behavior of this alloy in boiling distilled water can be described in exactly the same terms as was the corrosion of unalloyed uranium in air-saturated distilled water at room temperature. Ultimately local breakdown of the oxide film occurs, and the film does not form if oxygen is rigidly excluded from the water.

There are three mechanisms which appear reasonable as explanation for the effect of the alloying zirconium. In the first the incorporation of zirconium into the UO_2 lattice could make an inherently more stable film, and could also make the process of hydrogen migration through it more difficult. That this is at least reasonable is indicated by the fact that the presence of zirconium in the oxide produced on these alloys has been observed to reduce the UO_2 lattice dimensions.⁽¹⁵⁾

The second proposal for the protective action of zirconium is that the metallic zirconium in the surface layers of the metal acts as a getter for that hydrogen which does reach the metal surface. If, then, the zirconium is distributed in such fashion that it can getter all of the hydrogen reaching the surface, no uranium hydride should be formed, at least until the zirconium becomes saturated. According to this picture the ultimate breakdown of the oxide film occurs when this saturation is effected. The requirement for oxygen in the water might be that hydrogen can be absorbed by the zirconium at only a given rate. Reduction of the rate at which hydrogen reached the metal surface below this rate would be effected by the oxygen. If the amount of alloyed zirconium is increased so that the total rate at which this metal can absorb hydrogen at the surface is equal to or greater than the rate at which hydrogen gets there (without any retardation, as by oxygen), then there should be no requirement for dissolved oxygen. 7.5% zirconium is apparently sufficient for this purpose.⁽¹⁶⁾ Some gettering action by zirconium is indicated in uranium alloys, since it has been reported⁽⁴⁾ that as little as 0.5% zirconium virtually eliminates the formation of internal hydride crystals in gamma-phase alloys.

The third alternative considers that the quenched structure may consist of a single phase. If this is the case, it may be that the strained phase (martensitic) so produced allows rapid diffusion of hydrogen into it. Hence at least parts of the entire surface would be gettering the hydrogen. This proposal is in accord with the fact that the strained lattice has larger parameters than the normal alpha structure (Table IV). In other studies,^(19, 20) increasing lattice parameters (by tension) has been observed to cause the rate of hydrogen diffusion to increase, sometimes strikingly.

The altered properties of the oxide appear to be insufficient to explain all of the observed phenomena.⁽¹⁵⁾ The proposals relating to the disposal of hydrogen are therefore preferred and will be emphasized in the remainder of this discussion. Of these, the one based on the gettering action of the alloying elements is preferred. In addition to the observed gettering action of zirconium previously referred to, the greater effectiveness of increased percentages of zirconium seems more readily explained on the basis of this hypothesis.

The Role of Niobium

Just as in the corrosion of aluminum, where damage due to corrosion product hydrogen is believed to occur,⁽¹⁷⁾ the addition of cathodes having low hydrogen overvoltage to the metal surface should be beneficial. If all of the corrosion product hydrogen can be formed at these active cathode sites, and in a molecular form, it should bubble off and be lost from the uranium surface. The function of preventing access of the hydrogen to the uranium surface can thus be fulfilled in two ways: (1) the existence of hydrogen getter areas, and (2) the activity of cathodes having low

hydrogen overvoltage. It would be guessed that zirconium and niobium both act in the first way and that nickel, when present in the corroding solution, or as alloyed in the uranium, acts in the second way. In both cases, it is presumably necessary for the "hydrogen disposal units" to be present as second phase (with our choice of explanations in the preceding paragraph).

A fine random dispersion of the second-phase disposal units is desirable for their most efficient operation. The superiority of niobium over zirconium as an alloying constituent for this purpose is perhaps that it is better both as a hydrogen getter and as a grain refiner (which should provide finer distribution of the niobium or γ_2 phase).

Damage by Hydrogen

Presumably the niobium does not do a perfect job in providing protection. It is assumed that a small amount of hydrogen is available to the surface uranium. Very possibly this influences the corrosion rate, either by the formation of a small amount of uranium hydride or perhaps even by some disruption of the oxide by gaseous hydrogen formed beneath it.

When samples of the alloys described in this report are corroded in water they frequently become pock-marked or etched. Sometimes such localized corrosion is observed to make rather deep pits in the rolling direction of the material. This is perhaps an indication of the formation of surface hydride at the places where the hydride forms easiest. Subsequent to its formation the hydride presumably reacts with the water to form oxide corrosion product.

In addition, some of the hydrogen diffuses into the metal. Thus, for the "reference alloy" a constant rate of hydrogen pickup by corroding samples was observed, in terms of micrograms of hydrogen per square centimeter of corroding surface. It is presumably this latter hydrogen which causes ultimate failure of samples after prolonged corrosion exposure.

Consequently both reduction of the corrosion rate and increase of the corrosion lifetime might be caused by the use of more efficient material for hydrogen disposal, or greater area of such material, or its better distribution. In addition, it would be desirable to achieve the condition where that hydrogen which finds its way into the metal becomes uniformly distributed within it. In this way high local concentrations of hydrogen within the metal will not build up until such concentration has been reached throughout the metal. This should provide increased corrosion lifetimes over those now observed for the reference alloy. Both objectives are perhaps at least partly achieved in those alloys in which the gamma phase is stabilized. The body-centered, cubic gamma phase has a much higher multidirectional hydrogen diffusion rate than does the alpha uranium; it might also provide a more efficient surface for the reduction and liberation of

39

hydrogen. In a sense, the entire alloy is thus made an effective material for hydrogen disposal. Active cathodes on its surface should provide additional benefit, and apparently do (see corrosion in nickel salt solution and the effect of platinum).⁽³⁾

Hydrogen which is present in the metal appears to be harmful only if it is highly concentrated at certain locations. Thus, reference alloy as normally received shows only relatively short corrosion lifetime, when quenched without concurrent or previous vacuum treatment. This corrosion lifetime is considerably increased by the observed removal of gas, presumably hydrogen, by vacuum treatment at elevated temperature. Even alloy which has been loaded with hydrogen while in the gamma phase shows reasonable corrosion lifetime as quenched. It is thus implied that the distribution of the hydrogen is important, since hydrogen is soluble in the gamma phase and thus may be expected to be uniformly distributed. This tolerance to hydrogen disappears, and the material has very brief corrosion lifetime, if it is aged prior to corrosion testing. It would seem that aging concentrates the hydrogen at specific sites and the resultant change in the lattice facilitates further rapid penetration of the structure by corrosion product hydrogen, resulting in the early failures observed. This line of reasoning leads to the interesting prediction that removal of concentrated hydrogen at temperatures low enough so that the lattice changes are not repaired would not improve the corrosion resistance.

Effect of Heat Treatment

To return to the "strained alpha" alloys, it appears that suitable second-phase material must be present and that optimum behavior for a given composition will be achieved only by a good dispersion of an optimum particle size, as will be indicated below.

It will be fruitful to consider the metallurgy of the uranium-niobium and uranium-niobium-zirconium systems. Holding these alloys in the gamma phase homogenizes them. Rapid quenching produces a martensitic structure. According to Dwight,⁽⁹⁾ quenching small samples of the reference alloy produces a structure in which only the single phase can be detected by optical metallography up to magnifications of 2000X. As based on the preferred theory developed here, it would be expected that tiny samples, if single phased, would not be corrosion resistant. This, however, is not the case; such samples behave in a normal manner. This result makes it necessary to believe that (a) there is a submicroscopic, hydrogen-absorbing phase present, or (b) hydrogen diffuses readily into the martensite, or (c) the theory requiring absorption of hydrogen into the surface of "good" alloys during corrosion does not apply.

Moderate aging completes the precipitation (if it was not already complete) and causes a slight growth of the second-phase particles already present. In this way the precipitate particles become large enough to act

40

as more perfect sites for hydrogen liberation or absorption. For the liberation of gaseous hydrogen the particle size should be optimum when a sufficient accumulation of hydrogen atoms can form on the cathodic particle to make and liberate gaseous hydrogen, avoiding contact with the matrix material. The requirement as a getter would be much the same. It is presumed that a certain number of hydrogen atoms must accumulate on the surface of a material before rapid absorption and diffusion occur; the optimum size for particles would be presumed to be that which is required to accommodate such hydrogen atoms on its surface.

Optimum corrosion behavior should thus be produced by the heat treatment that gives optimum second-phase distribution. Further aging would then result in the agglomeration of the precipitate into fewer larger particles, leaving larger areas of the matrix phase which must be "protected" by the hydrogen disposal phase. There is also a question whether hydrogen diffusion into the metal at the phase boundary regions (between matrix and precipitate) would become easier.

There are two ways to explain the beneficial effect of zirconium as an additive to the uranium-niobium binary alloy. In the first, the addition of several per cent of zirconium will act as a grain refiner and will very likely slow down agglomeration of the second phase during aging. Hence the distribution of the active phase will perhaps be more favorable initially and the unfavorable effects of overaging will be retarded.

The second explanation deals with the nature of the second phase formed. The equilibrium structure of the reference alloy consists of alpha uranium and about 10% γ_1 ,⁽⁹⁾ which is gamma uranium saturated with niobium and zirconium. The corresponding structure of the niobium binary alloy is alpha uranium and γ_2 , which is niobium saturated with uranium. γ_2 is not found in the ternary system. It is entirely possible that the final precipitation and/or agglomeration of the γ_1 phase take place at different rates from those from the corresponding processes for the γ_2 phase. Thus, if the growth of the particles of γ_1 is considerably slower at a given temperature than is the equivalent growth of particles of γ_2 , the increased resistance of the ternary alloy to the harmful effects of overaging is explained.

Niobium-Tin Ternaries

The niobium-tin alloys showed promise of being every bit as good with respect to corrosion resistance with or without aging as the reference alloy. That further work on this alloy system did not show the material to be living up to its promise was perhaps no more than an indication that the system is metallurgically unfavorable. Different parts of the same piece frequently had completely different sensitivity to aging, and showed different corrosion rates and sensitivity to failure by cracking. Perhaps the trouble has simply been inhomogeneity, either in terms of composition or in terms of metal structure. One of the problems has apparently been a tendency to crack upon quenching from the gamma phase.

41

ACKNOWLEDGMENT

The cooperation and interest of the following were of great aid in this study.

C. R. Breden and A. H. Roebuck of the Reactor Engineering Division, ANL, directed the experiments on the long-time corrosion tests.

G. Dragel performed the corrosion tests and is responsible for some of the photomicrographs.

E. J. Silk, on loan to the Metallurgy Division from Babcock and Wilcox, is responsible for some of the photomicrographs and aided in their interpretation.

42

APPENDIX

TABLE IA

Notebook Record

The work described in this report was originally recorded in the following notebooks:

187E

245E

527E

629E

666E

765E

43

TABLE IIA

Composition of Alloys Tested
Analyses by Chemistry Division, ANL

Alloy	Zr (%)	Nb (%)	Sn (%)	C (ppm)	N (ppm)	Si (ppm)	Crucible Material ⁽¹⁾
H 187 T	-	3.09	-	100	(240?)	20	Magnesia
B	-	2.95	-	90	(240?)		
H 189 T	-	6.13	-	130	145	40	Magnesia
B	-	5.90	-	90	160	20	
H 203 T	3.93	1.77	-	10	35	200	Magnesia
B	4.70	1.73	-				
H 282 T	-	3.44	0.61	56	49	40	Thoria
H 288 T	4.90	0.51	-	38	49	50	Thoria
H 289 T	4.85	1.06	-	43	31	40	Thoria
H 290 T	4.81	1.47	-	72	34	40	Thoria
H 311 T	5.11	2.07	-	42	51	20	Thoria
H 317 T	5.40	1.57	-	65	46	50	Magnesia
B	5.36	1.60	-	23	26	60	
H 350 T	-	3.19	0.53	56	87	40	Magnesia
B	-	3.17	0.51	78	83	40	
H 352 T	-	3.20	1.00	2300	108	60	Magnesia*
B	-	3.23	0.99	1600	123	60	
H 354 T	-	3.27	1.60	259	103	60	Magnesia*
B	-	3.20	1.66	110	93	60	
H 356 T	-	3.12	0.26	60	50	70	Magnesia
B	-	3.11	0.25	53	15	60	
H 357 T	-	3.15	0.76	53	38	70	Magnesia
B	-	3.13	0.81	53	32	70	
H 416 T	4.88	1.71	-	25	11	100	Graphite
B	4.81	1.67	-	22	10		
H 419 T	5.80	1.80	-	15	13	200	Graphite*
B	4.95	1.62	-	78	34	150	
L 157 T	7.00	1.60	-	64	415	100	Magnasite*
B	6.00	1.65	-	43	134	100	
L 170 T	5.70	1.95	-	12	10	100	Magnasite*
B	5.20	1.60	-	21	16		

⁽¹⁾Most casting was done into a water cooled copper mold;

*denotes those which were cast into heated graphite molds.

BIBLIOGRAPHY

1. McWhirter, J. W. and Draley, J. E. "Aqueous Corrosion of Uranium and Alloys: Survey of Project Literature." ANL-4862 (May 1952).
2. Waber, J. T., "A Review of the Corrosion of Uranium and Its Alloys." LA-1524 (Nov 1952).
3. McGeary, R. K., et al. "Development and Properties of Uranium Base Alloys Corrosion Resistant in High Temperature Water. Part I - Alloys without Protective Cladding." WAPD-127 (April 1955).
4. Cawthorne, E. W. et al. "Corrosion in 650°F Degassed Water of Uranium-Molybdenum Alloys Containing Impurity Additions." BMI-1045 (Oct. 1955).
5. Draley, J. E. "Preliminary Report on Low Columbium: Uranium Corrosion Resistant Alloys." ANL-5078 (June 1953).
6. Carson, N. J. Jr., Baird, J. E., and Macherey, R. J. "Development of Methods for Making and Casting Uranium-Rich Zirconium-Niobium Alloys." ANL-5627, to be published.
7. Bean, C. H., Lindgren, J. R., and Macherey, R. J. "Roll Cladding Uranium-Zirconium and Uranium-Zirconium-Niobium Alloys with Zircaloy-2 for Plate Type Fuel Elements." ANL-5628, to be published.
8. Macherey, R. J., Bean, C. H., Lindgren, J. R., and Carson, N. J., Jr. "Manufacture of Fuel Plates for the Experimental Boiling Water Reactor." ANL-5629, to be published.
9. Dwight, A. E. and Mueller, M. "The Constitution of the Uranium-Niobium Binary and the Uranium-Zirconium-Niobium Ternary Alloys." ANL-5581, to be published.
10. Dwight, A. E. "Kinetic Transformations in the Uranium Rich Uranium-Niobium and Uranium-Niobium-Zirconium Alloy Systems." ANL-5582, to be published.
11. Kittel, J. H., Greenberg, S., Paine, S. H., and Draley, J. E. "Effects of Irradiation on Some Corrosion-Resistant Fuel Alloys." Nuclear Science and Engineering, to be published.
12. Greenberg, S. and Draley, J. E. "Effect of Irradiation on Corrosion Resistance of Some High Uranium Alloys." Nuclear Science and Engineering, to be published.

45

13. Breden, C. R. Unpublished data.
14. Pray, H. A. and Berry, W. E. "Corrosion of Uranium Alloys in High Temperature Water." BMI-874 (Oct. 1953).
15. Draley, J. E., McWhirter, J. W., Field, F., and Guon, J. "The Corrosion of Low Zirconium-Uranium Alloys in Boiling Water." ANL-5030 (April 1953).
16. Mueller, M., Private Communication (May 1955).
17. Draley, J. E. and Ruther, W. E. "Aqueous Corrosion of Aluminum: Methods of Protection Above 200°C," Corrosion, 12 480t (1956).
18. Draley, J. E. and Ruther, W. E. "Some Unusual Effects of Hydrogen in Corrosion Reactions." Journal of the Electrochemical Society, to be published.
19. Smith, Donald P., "Hydrogen in Metals," Chicago. University of Chicago Press (1948).
20. Burkart, M. W. (editor). "The Corrosion Mechanisms of Uranium Base Alloys in High Temperature Water." WAPD-127-Part III (Oct. 1956).