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THE CORROSION BEHAVIOR OF URANIUM-BASE
U-Nb, U-Nb-Zr, AND U-Mo ALLOYS IN
HYDROCHLORIC ACID AND OCEAN WATER

James M. Macki
Robert L. Kochen

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The Corrosion Behavior of Uranium-Base U-Nb, U-Nb-Zr, and U-Mo Alloys in Hydrochloric Acid and Ocean Water

James M. Macki and Robert L. Kochen

Abstract: The corrosion rates and products for depleted uranium (Tuballoy), U-4.5 wt% Nb, U-6 wt% Nb, U-8 wt% Nb, U-7.5 wt% Nb-2.5 wt% Zr (Mulberry), and U-10 wt% Mo were measured in ASTM ocean water at 26°C, 1N hydrochloric acid (HCl) at 26°C, and 0.1N HCl at 70°C. The six alloys tested, listed in order of increasing corrosion resistance to ocean water, are: Tuballoy, U-4.5 Nb, U-6 Nb, U-8 Nb, Mulberry, and U-10 Mo. In 1N HCl at 26°C the alloys, in order of increasing corrosion resistance, are: Tuballoy, U-4.5 Nb, U-6 Nb, U-10 Mo, Mulberry, and U-8 Nb. In 0.1N HCl at 70°C the positions of U-8 Nb and Mulberry are reversed from those given for 1N HCl.

INTRODUCTION

Uranium alloys are being developed to achieve high strength and good corrosion resistance while still preserving the nuclear and other desirable physical properties of pure uranium. Among the alloys of interest are U-4.5 wt% Nb*, U-6 wt% Nb, U-8 wt% Nb, U-7.5 wt% Nb-2.5 wt% Zr (Mulberry), and U-10 wt% Mo. The U-Nb alloys are frequently referred to as "binary".

Most of the previous corrosion investigations have been concerned with pure depleted uranium (Tuballoy) and enriched uranium alloys for nuclear reactor applications. The published work on Tuballoy corrosion indicates that Tuballoy is oxidized readily by water and water vapor even at room temperature.^{1,2} The corrosion rates in saturated water vapor (100% relative humidity) and full immersion in water are equivalent.^{3,4,5,6}

Both the Tuballoy-water and the Tuballoy-water vapor reactions are inhibited by oxygen;^{1,4} it has also been reported that CO₂ inhibits the Tuballoy-water vapor reaction and it is likely that carbonate ions act similarly in aqueous reactions.¹ The net reaction between Tuballoy and water or water vapor is^{1,4,7}

*U-4.5 wt% Nb designates the U-Nb binary alloy containing 4.0 to 4.7 wt% Nb and averaging 4.2 wt% Nb.

The amount of hydrogen gas generated by the uranium-water vapor reaction is 90 to 95% of the theoretical amount;^{3,7} the solid corrosion product is UO₂ . 08 ± 0.02 containing 2 to 9 wt% UH₃.^{1,4}

When Tuballoy is exposed to water vapor and oxygen simultaneously, the reaction mechanism has been described as

Thus, oxygen in the gas phase does not react directly with the metal but reacts with the hydrogen generated by the uranium-water vapor reaction to replace the water that has reacted.^{3,4,5,7}

Orman⁶ studied the corrosion of Tuballoy in water and water vapor in the temperature range from 35 to 100°C. It was observed that oxygen inhibited and hydrogen accelerated the uranium-water and uranium-water vapor reactions. Orman's results show that, in the absence of permanent gases, the reaction between Tuballoy and water vapor is not autocatalytic and there is no change in reaction rate on passing from saturated vapor to water immersion conditions. The Arrhenius plot for the temperature range from 35 to 100°C was linear, and thus Orman concluded that the reaction mechanism was invariant over this temperature range. Hence, the data indicate that accelerated tests are justified and can be extrapolated to lower temperatures within the same temperature range (35 to 100°C).

Mollison, English, and Nelson⁸ observed that the corrosion rates of uranium in distilled water at 50 and 100°C (boiling) are different for hydrogen-saturated and oxygen-saturated water. In aerated distilled water, the corrosion is initially less than in hydrogen-saturated water, probably because of the formation of protective oxide films. However, after relatively long times, the reaction rate in aerated distilled water increases, apparently approaching that observed in hydrogen-saturated (deaerated) water.

Baker, Less, and Orman⁹ also observed that Tuballoy exhibits linear corrosion kinetics when immersed in aqueous solutions at various pH values. No breakaway corrosion was observed over the pH range from 0.85 to 13.6, and the highest corrosion rate occurred in the 2.5 to 7.0 pH range. They concluded that the corrosion of Tuballoy by water does not proceed by an electrochemical mechanism and that the reaction is ionic in nature and probably involves diffusion of the hydroxyl ion. The corrosion rates in acetic, nitric, and sulfuric acids are equivalent at corresponding pH values, and similar equivalence applies in the alkaline region with sodium and potassium hydroxide, and aniline. Thus, the corrosion rate of Tuballoy in aqueous solutions is dependent on pH and not on the other ionic species present under the conditions of the experiments by Baker, Less, and Orman. However, using an electrochemical technique, Kindlimann and Greene¹⁰ found that the addition of chloride ions to sulfuric acid increased the dissolution rate of uranium at all potentials and caused shallow pits on the Tuballoy surface. They noted that the dissolution of Tuballoy in nitric and sulfuric acids was unusual in that, unlike most metals, the dissolution of uranium is retarded as the acid concentration is increased. It was observed that hydrogen ions and, to a lesser extent, sulfate and nitrate ions, inhibit dissolution. (Although hydrogen and nitrate ions suppress the dissolution reaction, concentrated nitric acid rapidly corrodes uranium; this has been hypothesized to be a direct result of the oxidizing characteristics of nitric acid.) The inhibiting effect of the nitrate and sulfate anions was observed by Kindlimann and Greene but not by Baker, Less, and Orman because Kindlimann and Greene used sensitive potentiostatic techniques, whereas Baker et al. used a less precise gravimetric technique. In 1*N* and 10*N* H₂SO₄, and in 2*N* and 5*N* HNO₃, Kindlimann and Greene observed that uranium dissolves in the hexavalent state as uranyl ions.

They suggest that the dissolution process occurred as a series of oxidation steps represented simply as

which yield the overall half-cell reaction

This mechanism is based on anodic polarization measurements in which the complementary cathodic

reactions occur at a platinum electrode connected to the Tuballoy anode via a potentiostatic circuit.

Draley, Greenberg, and Ruther¹¹ investigated the corrosion of U-3 wt% Nb and U-6 wt% Nb water contained in a high-temperature autoclave. They observed that both the U-3 wt% Nb and the U-6 wt% Nb alloys exhibit optimum corrosion resistance to water in the range from 100 to 300°C when the alloys were in the gamma-quenched condition. Aging gamma-quenched U-6 wt% Nb at 350°C doubled the corrosion rate of this alloy in degassed, distilled water at 260°C. The presence of dissolved oxygen in water at 290°C did not affect the corrosion rate of the gamma-quenched U-6 wt% Nb alloy.

Wabcr¹² measured the gravimetric corrosion rates of U-2 wt% Nb, U-4 wt% Nb, and U-6 wt% Nb alloys (quenched from 850°C in water) in 50% relative humidity air at 75°C. The corrosion rates of the U-2, -4, and -6 wt% Nb alloys were about 2, 1, and 0.5% respectively, of the corresponding corrosion rate of Tuballoy.

Since the published literature, as summarized above, does not contain sufficient data on the corrosion behavior of U-Nb binary alloys, this present investigation was initiated to determine the corrosion behavior of U-Nb binary alloys and to compare this corrosion behavior with that of Mulberry (U-7.5 wt% Nb-2.5 wt% Zr) and the U-10 wt% Mo alloy.

EXPERIMENTAL

The specimens for the immersion corrosion tests were 1-inch diameter by 0.080-inch-thick disks having a total surface area of 1.82 in² (11.7 cm²). The alloys tested were: depleted uranium (Tuballoy), U-4.5 wt% Nb, U-6 wt% Nb, U-8 wt% Nb, U-7.5 wt% Nb-2.5 wt% Zr (Mulberry), and U-10 wt% Mo. The disks were machined from hot-rolled sheet material produced from ingots that had been homogenized for 6 hours at 1100°C in a vacuum after vacuum induction melting and casting. All the alloys, except Tuballoy, were in the solution-quenched (unaged) condition. The solutionizing temperatures were 850°C for Mulberry and 800°C for the binary alloys. In the solution-quenched condition, the Mulberry and the U-8 Nb alloys probably exist in the tetragonal γ^0 structure whereas the U-4.5 Nb

and U-6 Nb alloys exhibit the alpha-double-prime (α'') structure. The U-10 Mo alloy possesses the gamma (γ) structure.

The surfaces of the disks were prepared by grinding the faces with 240-grit silicon carbide abrasive on a belt grinder using distilled water as a coolant. The curved edges of the disks were left in the as-machined condition.

The dimensions of the ground disks were measured with a micrometer to the nearest 0.001 inch. After measuring, the disks were cleaned with acetone, dried, and weighed to the nearest 0.1 mg.

Each weighed disk was placed on a glass holder and immersed in 400 ml of corrodent contained in a 500-ml tall-form beaker loosely covered with a Petri dish. The 400 ml of corrodent provided a volume-to-surface area ratio of 220 ml/in² conforming to NACE standard test method TM-01-69. The glass holder held the specimens in the center of the beaker one inch above the bottom with the disk faces inclined 30 degrees from vertical. During the exposure periods, the liquid levels in the beakers were maintained at 400 ml by daily additions of distilled water. The pH of each solution was measured before and after each test. The disks were immersed in the following environments: 0.1N HCl at 26 $\pm$ 2°C, 0.1N HCl at 70 $\pm$ 2°C, and ocean water at 26 $\pm$ 2°C. The ocean water was prepared according to ASTM designation D-1141-52. No attempt was made to control aeration in the corrodents; the solutions were exposed to air before and during the exposure period.

At the end of each exposure period, which varied from 1 to 30 days, the disks were removed from the corrodents and rinsed in running tap water while being rubbed with a rubber stopper to remove loose corrosion products. The rinsed disks were dried and reweighed to determine the weight losses. The weight losses were converted into two corrosion rate designations according to the equations

$$\begin{aligned} \text{mdd} &= \frac{\Delta W}{A T} \\ \text{mpy} &= \frac{(534) \Delta W}{D A' T'} \end{aligned}$$

where mdd is the corrosion rate in (mg)/(dm² day), mpy is the corrosion rate in mils penetration per year, ΔW is the weight loss in mg, A is the surface area in cm², A' is the surface area in in², T is the

exposure time in days, T' is the exposure time in hours, and D is the density in g/cm³.

The mdd designation is useful in research work because small differences in actual corrosion rates are more evident. The mpy designation is more useful for engineering applications because it indicates the life of a uniformly corroding structure. Since the mpy designation includes densities, it is more useful for comparing different alloys than the mdd designation which intrinsically favors low-density materials.

Actual disks, and turnings obtained when the disks were machined, were analyzed for composition and impurities. The corrosion products, which were removed from U-Nb binary alloy disks after 10-day exposure to 0.1N HCl at 70°C, were combined with the corresponding corrodent remaining after the tests, and were then filtered. To provide sufficient material for analysis, the corrosion products and corrodent from duplicate tests on the same alloy were combined. The compositions of the filtrates and residues were then analyzed. Selected corroded disks were also subjected to metallographic analysis.

Before the 10-day immersion tests in 0.1N HCl at 70°C, the edges of duplicate U-Nb binary alloy disks were coated with RTV[®] 3145 (Dow Corning) silicone adhesive to prevent corrosion of the more susceptible edges. Corrosion rates, based on only the exposed faces, were calculated and compared with similarly exposed, uncoated disks.

In one case, the edge and both faces of one U-4.5 Nb disk were ground with 240-grit abrasive and exposed to the corrodent. The corrosion rate and visible effects of this disk were compared with those of similarly exposed disks with only the faces ground.

To determine whether the 0.1N HCl solution became less corrosive with exposure, fresh U-Nb binary alloy disks were immersed for one day in the solution previously used for the 6-day tests; the corrosion rates were compared to the corresponding rates for one-day immersion in fresh corrodant.

The weight losses (mg/cm²) for the zero to 10-day tests in 0.1N HCl were plotted as a function of the exposure period. A least-

squares calculation was made to define a linear weight-gain curve and the corresponding slope for each alloy. The data for the edge-coated disks and the disks immersed for one day in the 6-day old solution were not included in the least-squares calculations.

RESULTS

The results of the composition and impurity analyses, of the uranium alloy samples, are summarized in Tables I and II, respectively.

The results of the gravimetric immersion tests are summarized in Tables III, IV, and V, and in Figures 1 to 6.

Photomicrographs of selected specimens are shown in Figures 7 to 14. The slopes of the curves in Figures 1 to 5 are given in (mg)/(cm² day). In Figure 6 and in Table V, the (mg)/(cm² day) corrosion rates have been multiplied by 100 to yield the more common mdd, (mg)/(dm² day), corrosion rate units. The mdd values have also been converted into mpy corrosion rate units in Table V.

TABLE I. Composition Analyses of Uranium Alloys.

Alloy	Composition (wt%)		
	Nb	Zr	Mo
U-4.5 Nb	4.2 ^a	—	—
U-6 Nb	5.7 ^b	—	—
U-8 Nb	7.7 ^c	—	—
Mulberry	7.5 ^d	2.44 ^d	—
U-10 Mo	—	—	9.4 ^e

^aAverage of 12 samples; Nb concentrations reported ranged from 4.0 to 4.7 wt%.

^bAverage of 10 samples; Nb concentrations reported ranged from 5.4 to 6.0 wt%.

^cAverage of 10 samples; Nb concentrations reported ranged from 7.2 to 8.4 wt%.

^dAverage of 3 samples; Nb concentrations reported were 7.4, 7.6 and 7.6 wt% while Zr concentrations reported were 2.43, 2.44 and 2.44 wt%, respectively.

^eAverage of 3 samples; Mo concentrations reported were 9.2, 9.5, and 9.6 wt%.

TABLE II. Typical Impurity Levels in the Uranium Alloys.

Impurities	Uranium Alloy (wt%)				
	(ppm) U-4.5 Nb ^a	U-6 Nb ^a	U-8 Nb ^a	Mulberry	U-10 Mo
Al	15	15	15	125	5
B	< 1	< 1	< 1	< 1	< 1
Ba	<100	<100	<100	< 50	< 10
Be	< 1	1	1	6	25
Bi	< 10	< 10	< 10	< 10	< 10
Ca	< 25	< 25	< 25	10	< 1
Cd	< 25	< 25	< 25	< 10	—
Co	< 10	< 10	< 10	< 10	< 10
Cr	< 50	< 50	< 50	10	< 10
Cu	20	25	15	30	15
Fe	40	50	60	100	10
K	< 10	< 10	< 10	10	< 1
Li	< 1	< 1	< 1	< 1	< 1
Mg	< 1	< 1	< 1	< 10	< 1
Mn	< 10	< 10	< 10	< 10	11
Mo	< 10	< 10	< 10	230	—
Ni	< 25	25	25	15	10
Pb	< 1	< 1	< 1	< 1	< 1
Sb	< 10	< 10	< 10	< 10	< 10
Si	58	73	30	600	90
Sn	< 1	< 1	< 1	< 10	15
Ti	< 50	< 50	< 50	<100	< 1
V	< 10	< 10	< 10	< 10	< 1
Zn	< 50	< 50	< 50	< 50	< 50
Zr	—	—	—	—	—
C	90	100	60	—	—
Nb	—	—	—	—	<100

^aThe Fe and Si contents in the U-Nb binary alloys were determined by atomic absorption.

TABLE III. The Results of the 30-Day Immersion Tests in ASTM Ocean Water at 20±2°C.

Alloy	Average Corrosion Rate ^a	
	mdd ^b	mpy ^c
Tuballoy	52	4
U-4.5 Nb	21	2
U-6 Nb	13	1
U-8 Nb	4	0.4
Mulberry	2	0.2
U-10 Mo	0.2	0.01

^aAverage of duplicate tests.

^bmdd = (mg)/(dm² day).

^cmpy = mils penetration per year.

TABLE IV. The Results of the 30-Day Immersion Tests in 1N HCl at $26 \pm 2^\circ\text{C}$.

Alloy	Average Corrosion Rate ^a	
	mdd ^b	mpy ^c
Tuballoy	Dissolved	
U-4.5 Nb	64	5
U-6 Nb	34	3
U-8 Nb	4	0.4
Mulberry	25	2
U-10 Mo	41	2

^aAverage of duplicate tests.^bmdd = (mg)/(dm² day).^cmpy = mils penetration per year.**TABLE V. The Corrosion rates of Uranium Alloys in 0.1N HCl at $70 \pm 2^\circ\text{C}$.**

Alloy	Corrosion Rate ^a	
	mdd ^b	mpy ^c
U-4.5 Nb	240	20
U-6 Nb	190	16
U-8 Nb	56	5
Mulberry	23	2
U-10 Mo	150	13

^aCorrosion rates were calculated from slopes of the least-squares curves in Figures 1 through 5.^bmdd = (mg)/(dm² day).^cmpy = mils penetration per year.**FIGURE 1. The Corrosion of U-4.5 wt% Nb in 0.1N HCl at $70 \pm 2^\circ\text{C}$.** **Legend**

- Data used to calculate least-squares curve.
- ◇ One-day immersion of fresh disk in solution used for 6-day test.
- Edges of disks coated with silicone adhesive — only faces of disks exposed to corrodent.
- △ In addition to the faces, the edge of the disk was abraded prior to exposure.

FIGURE 2. The Corrosion of U-6 wt% Nb in 0.1N HCl at $70 \pm 2^\circ\text{C}$. **Legend**

- Data used to calculate least-squares curve.
- ◇ One-day immersion of fresh disk in solution used for 6-day test.
- Edges of disks coated with silicone adhesive — only faces of disks exposed to corrodent.

FIGURE 3. The Corrosion of U-8 wt% Nb in 0.1N HCl at 70±2°C.

FIGURE 5. The Corrosion of U-10 wt% Mo in 0.1N HCl at 70±2°C. (Curve determined by least-squares calculation.)

FIGURE 4. The Corrosion of Mulberry in 0.1N HCl at 70 ±2°C. (Curve determined by least-squares calculation.)

FIGURE 6. A Comparison of the Corrosion Kinetics of Uranium Alloys in 0.1N HCl at 70+2°C (Corrosion rates, calculated from Least-squares slopes, are adjacent to each curve.)

TABLE VI. Analyses of the Corrosion Products and Corrodent Solutions After 10 Days Immersion of Duplicate Disks in 0.1N HCl at 70 $\pm$ 2°C.

Alloy	Filtrate ^a (mg/ml)		Residue ^b	
	Uranium	Niobium	Major	Minor
U-4.5 Nb	345	<1	UO ₂	α U
U-6 Nb	305	<1	UO ₂	α U
U-8 Nb	68	<1	UO ₂	α U
Mulberry ^c	—	—	UO ₂	None
U-10 Mo ^{c,d}	—	—	UO ₂	None

^aUranium and niobium analyses were by emission spectroscopy.

^bResidue analyses were by X-ray diffraction.

^cX-ray diffraction analyses results from the surfaces of corroded disks (no duplicates).

^dA rust-colored precipitate, identified as MoO₃, formed on the bottom of the beaker.

X-ray diffraction and X-ray fluorescence analyses of the corroded U-Nb binary alloy specimens and the corresponding loose corrosion products showed that the corrosion products were UO₂. No niobium or chloride compounds were detected for any of the uranium alloys tested. A red (rust colored) corrosion product precipitated during the U-10 Mo corrosion tests in 0.1N HCl; the red precipitate was identified by X-ray diffraction to be MoO₃. The results of the analyses of the corrosion products and corrodent solutions after 10-days immersion in 0.1N HCl at 70°C are summarized in Table VI.

DISCUSSION

The results of the immersion tests in the three environments tested (0.1N HCl, 1N HCl, and ocean water) show that the corrosion resistances of U-Nb binary alloys progressively increase with Nb content up to the highest Nb content tested, 8 wt%. This is in agreement with the earlier work of Briggs¹³ in 0.1N HCl at 70°C. As shown in Table III, adding 4.5 wt% Nb decreases the corrosion rate in ocean water to less than 50% of the corrosion rate of

Tuballoy. Tuballoy dissolves in 1N HCl at room temperature in less than 4 days (Table IV) while U-4.5 Nb exhibits a moderate corrosion rate of 5 mpy in the same environment.

The increased Nb content in the U-6 Nb alloy further decreases the corrosion rate (with respect to that of the U-4.5 Nb alloy) by 50, 40, and 20% in the ocean water, 1N HCl and 0.1N HCl environments, respectively. The U-8 Nb alloy exhibits corrosion rates that are 60 to 90% less than the corresponding rates for the U-6 Nb alloy in the three environments tested. The corrosion resistance of the U-8 Nb alloy may be enhanced by both the higher Nb content and by the stabilization of the gamma-phase structure. The gamma phase is stabilized by the 8 wt% Nb; whereas, U-4.5 Nb and the U-6 Nb alloys exhibit the alpha-double-prime phase in the solution-quenched condition, the U-8 Nb and U-10 Mo alloys and Mulberry all possess the gamma structure in the solution-quenched condition.

The main compositional difference between the Mulberry and the U-8 Nb alloy is the 2.5 wt% Zr in the Mulberry; the average Nb content in the U-8 Nb alloy is 7.7 wt%, whereas that of the Mulberry is 7.5 wt% (Table I). The results summarized in Tables III and IV show that Mulberry exhibits a slightly better corrosion resistance than U-8 Nb in ocean water, but in 1N HCl the U-8 Nb alloy exhibits the lowest corrosion rate of the five alloys tested. The corrosion rate of Mulberry in 0.1N HCl is 50% less than that of U-8 Nb, indicating that the 2.5 wt% Zr in Mulberry may contribute to the corrosion resistance of the alloy in this environment. The corrosion rates of Mulberry and U-8 Nb in ocean water are not significantly different, but the much greater corrosion resistance of the U-8 Nb alloy in 1N HCl suggests that the 2.5 wt% Zr may be detrimental to the corrosion resistance of Mulberry in the 1N HCl environment. The differences in corrosion rates could also be attributed to variations in Nb content between the Mulberry and U-8 Nb alloys.

The U-10 Mo alloy exhibits a higher corrosion rate in 0.1N HCl at 70°C than do U-8 Nb and Mulberry (Table V); however, in ocean water, U-10 Mo exhibits the lowest corrosion rate of the five alloys tested (Table III). This is not an inconsistent result since the acid and ocean water environments are quite different; the ocean water has a pH of 8.2 and contains a large variety of components.

To relate the data from the longer immersion tests, it is necessary to verify that the corrodent solutions remain stable during the tests. First, the corrosion behaviors of the five uranium alloys in 0.1N HCl at 70°C (Figures 1-5) show that all of these alloys exhibit linear oxidation kinetics in an acid environment. Second, the weight losses for each U-Nb binary alloy (Figures 1-3) are equivalent after a one-day exposure both to fresh acid and to acid that had been used for 6-day immersion tests. In addition, the solutions exhibited a change of less than 0.2 pH units during the long exposure periods. These results indicate that the corrosivity of the acid does not change significantly during the immersion tests.

Figure 1 contains a datum point (triangular symbol) for the disk that was abraded on its edge in addition to the faces; all other disks were abraded only on the faces. Since the weight losses after two-days

FIGURE 7. Photomicrograph of a Transverse Section Through U-4.5 Nb Disk Showing Edge Corrosion (grooving) After 10 Days Immersion in 70°C, 0.1N HCl. 100X

FIGURE 8. Photomicrograph of Section Parallel to Faces of U-4.5 Nb Disk. 100X

exposure for the edge-abraded disk and the duplicate face-abraded disks were equivalent, it is concluded that abrading only the faces of the disks did not affect the subsequent corrosion kinetics.

After exposure to 0.1N HCl at 70°C for more than 6 days, the U-4.5 Nb and U-6 Nb alloy disks exhibited localized corrosion along the edges. This localized corrosion produced grooves along the curved edges of the specimens. Photomicrographs were obtained of cross-sections through disks which had been exposed to 70°C, 0.1N HCl for 10 days, and some photomicrographs are shown in Figures 7 and 10.

Figures 1, 2, and 3 contain data points (square symbols) for U-Nb alloy disks whose edges were coated with RTV[®] silicone adhesive (Dow Corning 3145). The edge-coated disks were exposed for the full 10-day period to maximize the effect of grooving on the uncoated disks. As shown in Figure 1, the datum point corresponding to the average weight loss for the two edge-coated disks would be nearly coincident with the least-squares curve for the U-4.5 Nb alloy. This indicates that the faces of the U-4.5 Nb alloy disks corrode at about the same rate as the edges in spite of the observed grooving on the

U-4.5 Nb disks. The edge-coated U-6 Nb and U-8 Nb disks, as shown in Figures 2 and 3, exhibited lower corrosion weight losses than either of the uncoated disks. This indicates that the edges of the disks corroded faster than the faces, as would be expected for disks machined from rolled plate. The photomicrographs in Figures 7 and 10 show that the edge or

grooving type of attack occurs mainly on the U-4.5 Nb disks and, to a lesser extent, on the U-6 Nb disks. No edge-grooving was observed on the U-8 Nb, Mulberry, or U-10 Mo disks. The microstructures shown in Figures 7 and 10 indicate that the edge grooving may be due to differential carbon concentrations, or possibly, to niobium segregation.

FIGURE 9. Photomicrograph of a Section Parallel to the Faces of a U-6 Nb Disk. 100X

FIGURE 11. Photomicrograph of a Section Parallel to the Faces of a U-8 Nb Disk. 100X

FIGURE 10. Photomicrograph of a Transverse Section Through a U-6 Nb Disk Showing Edge Corrosion (grooving) After 10 Days Exposure to 0.1N HCl at 70°C. 100X

FIGURE 12. Photomicrograph of a Transverse Section Through a U-8 Nb Disk after 10 Days Exposure to 0.1N HCl at 70°C. No Edge Grooving was Observed. 100X

FIGURE 13. Photomicrograph of a Transverse Section Through a U-10 Mo Disk. 100X

FIGURE 14. Photomicrograph of a Transverse Section Through a Mulberry Disk. 250X

CONCLUSIONS

1. U-4.5 Nb, U-6 Nb, U-10 Mo, U-8 Nb, and Mulberry (in that order of increasing corrosion resistance) exhibit linear corrosion kinetics in air-equilibrated 0.1N HCl at 70°C.
2. The edges of U-6 Nb and U-8 Nb disks, machined from rolled sheet, corrode slightly faster than the faces in 0.1N HCl at 70°C.
3. U-4.5 Nb disks, machined from rolled sheet, exhibit a preferential grooving type of attack along the edges, but the overall corrosion rates of the faces and edges are equivalent in 0.1N HCl at 70°C.
4. The six alloys tested, listed in their order of increasing corrosion resistance to ocean water are: Tuballoy, U-4.5 Nb, U-6 Nb, U-8 Nb, Mulberry, and U-10 Mo.
5. The six alloys tested, listed in their order of increasing corrosion resistance to 1N HCl at 26°C are: Tuballoy, U-4.5 Nb, U-6 Nb, U-10 Mo, Mulberry, and U-8 Nb.
6. The corrosion resistances of the U-Nb binary alloys, in the solution-quenched condition, increase with Nb content up to the highest value tested. The 8 wt% Nb alloy is the most resistant to corrosion in 0.1N HCl at 70°C, 1N HCl at 26°C, and ocean water at 26°C.
7. The corrosion rates of Mulberry in 70°C, 0.1N HCl and in 26°C ocean water are 50% less than the corresponding rates for U-8 Nb; however, in 26°C, 1N HCl, the corrosion rate of Mulberry is about five times greater than that of the U-8 Nb alloy.

REFERENCES

1. M. McD. Baker, L. N. Less, and S. Orman, *J. Faraday Soc.*, 1966, Vol. 62, p 2513.
2. J. E. Draley, *J. Electrochem. Soc.*, 1957, Vol. 104, p 329.
3. S. Orman and P. Walker, *J. Oil & Colour Chemist's Assoc.*, 1965, Vol. 48, p 233.
4. M. McD. Baker, L. N. Less, and S. Orman, United Kingdom Atomic Energy Authority, Report AWRE 0-45/65, July 1965.
5. M. McD. Baker, J. W. Bleloch, N. Less, and S. Orman, United Kingdom Atomic Energy Authority, Report AWRE 0-40/64, 1964.
6. S. Orman, United Kingdom Atomic Energy Authority, Report AWRE 0-94/63, December 1963.
7. S. Orman and P. Robertson, United Kingdom Atomic Energy Authority, Report AWRE 0-54/65, June 1965.
8. W. A. Mollison, G. C. English, and F. Nelson, Atomic Energy Commission, Report CT-3055, June 1945.
9. M. McD. Baker, L. N. Less, and S. Orman, United Kingdom Atomic Energy Authority, Report AWRE 0-44/65, July 1965.
10. L. E. Kindlimann and N. D. Greene, *Corrosion*, 1967, Vol. 23, p 29.
11. J. E. Draley, S. Greenberg, and W. E. Ruther, Argonne National Laboratory, Report ANL-5530, April 1957.
12. J. T. Waber, Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 6, p 204.
13. J. L. Briggs, unpublished data, Rocky Flats Division, The Dow Chemical Company, August 1968.