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THE EFFECTS OF TERNARY ALLOYING ADDITIONS
ON THE CORROSION RESISTANCE OF
EPSILON-PHASE URANIUM-ZIRCONIUM ALLOYS

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For The Atomic Energy Commission

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Chief, Declassification Branch

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THE EFFECTS OF TERNARY ALLOYING ADDITIONS
ON THE CORROSION RESISTANCE OF EPSILON-PHASE
URANIUM-ZIRCONIUM ALLOYS

James E. Reynolds, Warren E. Berry, Horace R. Ogden,
Robert S. Peoples, and Robert I. Jaffee

The corrosion rate in 680 F water of the uranium-50 w/o zirconium binary alloy was found to be $-0.20 \text{ mg}/(\text{cm}^2)(\text{hr})$, and that of the uranium-40 w/o zirconium binary alloy was $-0.34 \text{ mg}/(\text{cm}^2)(\text{hr})$. Both alloys corroded uniformly, with no evidence of discontinuous failure. Normal variations in interstitial content in either alloy had no significant effect on corrosion behavior. Tantalum additions, in the range of 0.2 to 5 w/o, improved the corrosion rate of the uranium-50 w/o zirconium base, with a minimum rate of $-0.06 \text{ mg}/(\text{cm}^2)(\text{hr})$ for the 5 w/o tantalum alloy. The 5 w/o tantalum addition to the uranium-40 w/o zirconium alloy decreased the corrosion rate of the base to $-0.11 \text{ mg}/(\text{cm}^2)(\text{hr})$ in the epsilonized condition only. In other conditions, the 5 w/o tantalum alloy failed discontinuously. All other additions to both bases either had no effect or decreased corrosion resistance. These included aluminum, chromium, iron, molybdenum, nickel, platinum, tin, titanium, tungsten, and vanadium additions.

INTRODUCTION

Uranium-zirconium alloys are a potential material for a pressurized water reactor. For this application, it is desirable to use as high a uranium content as possible, commensurate with adequate corrosion resistance. The results of a literature survey⁽¹⁾ indicated that uranium-zirconium alloys containing about 50 to 60 w/o uranium, when heat treated to form epsilon phase, offered possibilities for a high-uranium-content corrosion-resistant alloy. On the basis of this survey, and the probability that some alloying additions to the uranium-zirconium base would improve corrosion resistance, the research described in this report was undertaken as part of the AlW development program for WAPD.

Two uranium-zirconium compositions were chosen as the base alloys for this study: uranium-50 w/o zirconium and uranium-40 w/o zirconium. To these bases three types of alloying elements were added, for the reasons indicated below:

- (1) Elements which probably retard the beta-decomposition reaction and might retard the decomposition of the epsilon phase:

(1) References at end.

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Titanium
Chromium
Tin
Aluminum

- Platinum
Iron
Nickel

- Oxygen
Nitrogen
Carbon

EXPERIMENTAL TECHNIQUES

Alloy Compositions

Element	Amount Added to Indicated Base	
	Uranium-50 w/o Zirconium	Uranium-40 w/o Zirconium
Molybdenum	1, 5, 10 w/o	5 w/o
Tantalum	0.2, 0.5, 1, 5, 10 w/o	5 w/o
Vanadium	1, 5, 10 w/o	5 w/o
Titanium	1, 5, 10 w/o	5 w/o
Chromium	1, 5, 10 w/o	5 w/o
Tungsten	1, 2, 4 w/o	2 w/o
Aluminum	1, 2, 4 w/o	2 w/o
Tin	1, 2, 4 w/o	2 w/o
Platinum	0.5, 1, 2 w/o	1 w/o
Nickel	0.5, 1, 2 w/o	1 w/o
Iron	0.5, 1, 2 w/o	1 w/o

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Element	Amount Added to Indicated Base	
	Uranium-50 w/o Zirconium	Uranium-40 w/o Zirconium
Oxygen	100, 630, 1000 ppm	100, 630, 1000 ppm
Carbon	30, 60, 120 ppm	30, 60, 120 ppm
Nitrogen	60, 200, 300 ppm	60, 200, 300 ppm

Materials

The majority of the alloys studied were prepared from uranium-50 w/o zirconium and uranium-40 w/o zirconium master alloys. The master alloys were prepared from Grade A Bureau of Mines sponge zirconium and center-cut dingot uranium by consumable-electrode arc melting. The chemical analyses of the master alloys, listing the usual impurity elements, are given in Table 1.

TABLE 1. CHEMICAL ANALYSES OF THE MASTER ALLOYS

Nominal Alloy	Analyzed Uranium Content, w/o	Analyzed Impurity Content, ppm																		
		Al	Cu	Co	Cr	Fe	Mg	Mn	Mo	Ni	Pb	Si	B	Na	K	Li	Ca	M	O	N
Uranium-50 w/o Zirconium	49.8	5	60	<5	30	150	<2	25	45	14	30	6	<0.1	5	<5	<2	<2	18	630	60
Uranium-40 w/o Zirconium	59.8	5	10-400	<5	20	150	<2	17	10	28	10	5	<0.1	5	<5	<5	<2	45	690	60

Except for those containing nitrogen, the ternary alloys were prepared by additions to the master alloys and arc melting. Oxygen was added as UO_2 and carbon as UC. Nitrogen was added to nibbled master alloy in a modified Sieverts apparatus with subsequent arc melting.

Dingot uranium and crystal-bar zirconium were used to make high-purity binary alloys containing less than the commercial amounts of oxygen and nitrogen.

Arc-Melting Techniques

All alloys used in this investigation were arc melted in a tungsten-electrode rocking-hearth furnace under a helium pressure of approximately 15 cm of mercury. Approximately 100 grams of charge was used per melt.

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The melting procedure consisted of first evacuating the furnace chamber to a pressure less than 5μ of mercury and purging with helium at a pressure of about 15 cm. The system was re-evacuated to a pressure of less than 5μ and then filled with helium to a pressure of 15 cm. Each alloy was melted three times, inverted, and again melted three times. Arc amperage was approximately 300 amp, and each melting took approximately 1-1/2 min.

All as-cast buttons were radiographed and with few exceptions were found to be homogeneous. The alloys that showed some segregation were remelted (often several times) until they were homogeneous.

Fabrication

Arc-melted alloy buttons were hot rolled in air to approximately 100-mil sheet after heating to 1600 F in helium. The reductions were 10 to 20 per cent per pass, reheating between each pass.

The following alloys cracked badly during the first pass in hot-rolling attempts:

Uranium-50 w/o zirconium base containing

10 w/o vanadium
1, 2 w/o iron

Uranium-40 w/o zirconium base containing

1 w/o iron.

Also, the uranium-50 w/o zirconium-base alloy with 4 w/o aluminum edge cracked to the extent that about one-half of the alloy had to be discarded. An attempt was made to hot roll the uranium-50 w/o zirconium-base alloy with 1 w/o iron at 1700 F, but the ingot cracked badly with one pass.

Specimen Geometry

The hot-rolled sheet was cleaned by vapor blasting. Eight specimens measuring approximately 1.25 by 0.50 by 0.080 in. were cut from each alloy, using an abrasive cutoff wheel. Analytical samples were milled from the middle and ends of each strip.

In preparing cast specimens for corrosion tests, approximately 0.010 in. was machined from the top and bottom of each ingot, and the turnings used for chemical analysis. The corrosion-test specimens were approximately 0.90 by 0.25 by 0.20 in.

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The specimens for electrical-resistance measurements were prepared by hand and were approximately 1 by 0.1 by 0.1 in. Accurate dimensional control was unnecessary, since specific resistivity is not necessary in order to follow the aging response of an alloy.

Heat Treatment

Wrought alloys were corrosion tested in the following heat-treated conditions:

- (1) 800 C for 1 hr, water quenched without breaking Vycor tube*
- (2) 800 C for 1 hr, furnace cooled at approximately 6 F per min
- (3) Heat Treatment (2) above, plus 14 days at 550 C and air cooled
- (4) Heat Treatment (2) above, and 10 per cent reduction in thickness by rolling at 425 C, anneal 24 hr at 550 C, air cool, 10 per cent reduction in thickness by rolling at 425 C, and a final 24-hr anneal at 550 C with air cooling.

Cast alloys were corrosion tested in the following heat-treated conditions:

- (1) 800 C for 1 hr, water quenched, breaking Vycor tube
- (2) 800 C for 1 hr, furnace cooled at approximately 6 F per min
- (3) Heat Treatment (2) above, plus 24 hr at 580 C, air cooled.

The aging response of the following selected alloys was studied, using electrical-resistance measurements:

Uranium-50 w/o zirconium base containing

1, 10 w/o tantalum
0.5 w/o nickel
Binary control

Uranium-40 w/o zirconium base containing

300 ppm carbon.

*All heat treatments were carried out with the specimens sealed in a Vycor tube in a helium atmosphere.

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These alloys were held 1 hr at 800 C and water quenched, breaking the Vycor tube. Following this, the electrical resistance of each alloy was measured by interrupting the aging at 580 C (by quenching) after 10 min, 30 min, and 1, 10, 24, and 240 hr.

Testing Procedures

Hardness

Cross-sectional Vickers hardnesses were made with a 10-kg load applied. All specimens were mounted in Epon and wet polished through No. 2 grit emery. At least three measurements were made on each specimen, and an average taken for the hardness values reported. The hardnesses measured for a given specimen were approximately equal.

Metallography

Metallographic specimens were cut transversely from the strips subsequently subjected to corrosion tests. In addition, some micrographic studies were made of specimens after corrosion testing.

Electrical Resistance

As indicated previously, electrical-resistance measurements were made for the purpose of following the aging response of some of the alloys. For relative resistance changes, this does not require a knowledge of the specimen cross section or an accurately machined specimen. Only one specimen of each alloy of interest was used to determine the percentage change in resistance. This specimen was given a sequence of heat treatments with resistance measurements at certain time intervals. Thus, one important restriction is imposed upon the method of measurement, i.e., the voltage probing must be reproducible if relative resistances of one specimen are to be obtained for the various stages of aging. A jig of Bakelite and brass with two sharp probes of heat-treated steel was constructed for these resistance measurements. The apparatus was used in conjunction with a Kelvin bridge capable of measuring resistance to approximately 10^{-6} ohm. Five to ten resistance measurements were made for each value reported. Each specimen was removed from the jig and repositioned prior to each resistance measurement. Data showed that, with this procedure, the error in probing was less than ± 0.5 per cent. With the specimen geometry as previously indicated and the voltage probes spaced 0.862 in. apart, the resistances were of the order of 10^{-3} ohm.

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Corrosion

Corrosion tests were conducted in 1-liter Type 316 stainless steel autoclaves in static degassed water at 680 ± 10 F. Water was once distilled and then passed through an ion-exchange bed to insure specific resistivity greater than 1 megohm-cm. The water was degassed by boiling for at least 1 hr. The test autoclave was completely filled with water while the water was still boiling. The autoclave was quickly sealed and inserted in a heating jacket. While the autoclave was coming to temperature, a measured amount of water was bled off to further purge the system and to insure adequate headspace. The headspace in each autoclave contained a palladium diffusion valve to remove excess hydrogen resulting from corrosion. The valve was patterned after an early model designed at WAPD.⁽²⁾

Test samples were shaper-finished to 0.060 in. thick by approximately 0.5 in. wide and 1.0 in. long. Samples were measured, degreased, weighed, and placed in Chromel A wire baskets. The baskets were in electrical contact with the autoclave during corrosion testing. Samples were examined after 1, 3, and 7 days of exposure and once every 7 days thereafter. After each exposure period, the samples were oven-dried at 140 F and the loosely adherent oxide was brushed off prior to weighing.

PRESENTATION AND DISCUSSION OF RESULTS

Corrosion results, obtained in 680 F degassed water with cast, wrought, and heat-treated alloys, showing the effects of compositional variables, are presented in Tables 2, 3, 4, and 5 along with hardnesses and microstructures. In addition to the analyses for ternary additions given in Tables 2, 3, 4, and 5, the alloys containing oxygen and nitrogen additions were more completely analyzed. Results of these analyses are given below:

Alloy	Nominal Composition, w/o		Chemical Analysis, ppm				Intended Inter- stitial Content, ppm
	U	Zr	O	N	C	H	
BB-35	50	50	860	50	70	47	Base alloy
BB-34	50	50	959	50		83	1000 O
BB-36	50	50	158	30		42	100/200 O ^(a)
BB-37	50	50	730	180		80	120N
CC-13	60	40	996	50	60	63	Base alloy
CC-12	60	40	893	50		79	1000 O
CC-14	60	40	110/87	30		28/29	100 O ^(a)
CC-15	60	40	632	130		55	120N

(a) Alloys made with crystal-bar zirconium and dingot uranium.

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TABLE 2. CORROSION RESULTS OBTAINED ON URANIUM-50 w/o ZIRCONIUM-BASE ALLOYS TESTED IN 680 F DEGASSED WATER

Alloy	Alloy Content, w/o				Corrosion Results for Indicated Testing Condition ^(a)									
	Nominal		Addition		Condition 1 ^(b)		Condition 2 ^(c)		Condition 3		Condition 4		Condition 5	
	Uranium	Zirconium	Nominal	Actual	Rate ^(d)	Life ^(e)	Rate ^(d)	Life ^(e)	Rate ^(d)	Life ^(e)	Rate ^(d)	Life ^(e)	Rate ^(d)	Life ^(e)
					mg/(cm ² ·hr)	days	mg/(cm ² ·hr)	days	mg/(cm ² ·hr)	days	mg/(cm ² ·hr)	days	mg/(cm ² ·hr)	days
BB-35 ^(f)	50	50	630 ppm O	860 ppm O	-0.19	77-84	-0.18	56-63	-0.20	91-98	-0.21	91-98	-0.20	105-112
BB-1	49.5	49.5	1.0Mo	1.08Mo	-0.17	98-105	+0.03	3-7	-0.25	63-70	-0.37	49-56	-0.26	70-77
BB-2	47.5	47.5	5.0Mo	5.11Mo	-0.17	21-28	-0.17	7-14	-0.19	3-7	-	0-1	-0.27	7-14
BB-3	45.0	45.0	10.0Mo	10.2Mo	-0.004	1-3	-0.14	3-7	-11.0	1-3	-	0-1	-0.21	3-7
BB-3.25C	49.875	49.875	0.25Ta	0.2Ta	-0.09	21-28	-0.27	1-3	-0.16	>56	-0.15	>56	-	-
BB-3.5C	49.75	49.75	0.5Ta	0.5Ta	-0.04	21-28	-0.18	3-7	-0.13	>56	-0.12	>56	-	-
BB-4	49.5	49.5	1.0Ta	1.06Ta	-0.11	>154	-0.11	>133	-0.10	>133	-0.10	>112	-0.10	>112
BB-5	47.5	47.5	5.0Ta	5.0Ta	-0.06	>154	-0.05	>133	-0.06	>133	-0.10	>112	-0.09	>112
BB-6	45.0	45.0	10.0Ta	9.8Ta	-0.07	77-84	-0.09	14-21	-0.06	77-84	-0.10	>112	-0.04	35-42
BB-43C	49.5	49.5	0.5Ta 0.5Ni	0.07Ta 0.52Ni	+0.01	3-7	+0.74	3-7	-0.03	>56	+0.01	35-42	-	-
BB-7	49.5	49.5	1.0V	0.98V	-2.49	1-3	-1.43	3-7	-0.86	7-14	-0.42	21-28	-0.90	14-21
BB-8	47.5	47.5	5.0V	4.92V	-	0-1	-	0-1	-0.89	1-3	-1.59	3-7	-	0-1
BB-9C	45.0	45.0	10.0V	9.8V	-	-	-	-	-	-	-	-	-	-
BB-9C	45.0	45.0	10.0V	9.8V	-	0-1	-	0-1	-	0-1	-	0-1	-	-
BB-10	49.5	49.5	1.0Ti	1.0Ti	-10.9	1-3	-	0-1	-16.1	1-3	-	0-1	-13.9	1-3
BB-11	47.5	47.5	5.0Ti	4.4Ti	-	0-1	-	0-1	-	0-1	-	0-1	-	0-1
BB-12	45.0	45.0	10.0Ti	10.3Ti	-0.02 ^(g)	63-70	-1.04	7-14	-2.47	1-3	+0.42	7-14	-0.001	1-3
BB-13	49.5	49.5	1.0Cr	0.69Cr	-0.26	35-42	-0.23	21-28	-0.20	56-63	-0.21	84-91	-0.19	70-77
BB-14	47.5	47.5	5.0Cr	4.61Cr	-0.44	35-42	-0.44	21-28	-0.33	35-42	-0.32	42-49	-0.43	14-21
BB-15	45.0	45.0	10.0Cr	9.73Cr	-0.84	21-28	-0.17	14-21	-0.86	14-21	-0.33	42-49	-	0-1
BB-16	49.5	49.5	1.0W	0.4W	-0.14	49-56	-0.25	28-35	-0.20	49-56	-0.22	56-63	-0.20	42-49
BB-17	49.0	49.0	2.0W	1.05W	-0.77	28-35	-0.18	14-21	-0.22	28-35	-0.23	35-42	-0.20	28-35
BB-18	48.0	48.0	4.0W	2.64W	-0.08	14-21	-0.16	7-14	-0.21	21-28	-0.23	28-35	-0.20	28-35
BB-19	49.5	49.5	1.0Al	0.96Al	-	0-1	-11.1	1-3	-1.02	14-21	-0.57	14-21	-2.58	3-7
BB-20	49.0	49.0	2.0Al	1.98Al	-5.43	1-3	-11.4	1-3	-1.05	7-14	-2.54	3-7	-1.38	1-3
BB-21	48.0	48.0	4.0Al	4.0Al	-3.81	1-3	-8.32	1-3	-4.58	1-3	-	0-1	Not tested	
BB-22	49.5	49.5	1.0Sn	0.95Sn	-0.36	28-35	-0.37	28-35	-0.35	49-56	-0.37	35-42	-0.35	28-35
BB-23	49.0	49.0	2.0Sn	1.97Sn	-0.30	21-28	-0.36	14-21	-0.37	42-49	-0.37	35-42	-0.43	28-35
BB-24	48.0	48.0	4.0Sn	3.82Sn	-0.62	3-7	-1.07	7-14	-0.84	14-21	-0.62	14-21	-0.99	7-14
BB-25	49.75	49.75	0.5Pt	0.5Pt	-0.25	98-105	-0.25	77-84	-0.19	56-63	-0.06	14-21	-0.18	21-28
BB-26	49.5	49.5	1.0Pt	0.88Pt	-0.21	98-105	-0.37	35-42	+0.02	56-63	-0.21	35-42	+0.03	14-21
BB-27	49.0	49.0	2.0Pt	1.93Pt	-0.20	105-112	-0.28	84-91	+0.04	35-42	-0.12	21-28	+0.03	14-21
BB-28	49.75	49.75	0.5Ni	0.53Ni	+0.01	42-49	+0.04	28-35	-0.09	21-28	-0.05	21-28	-0.15	21-28
BB-29	49.5	49.5	1.0Ni	0.95Ni	+0.03	42-49	+0.03	35-42	-0.22	56-63	-0.29	14-21	-0.32	7-14
BB-30	49.0	49.0	2.0Ni	1.94Ni	+0.04	28-35	+0.04	21-28	-0.11	7-14	-0.17	7-14	-1.15	7-14
BB-31	49.75	49.75	0.5Fe	0.48Fe	-0.13	63-70	-0.16	63-70	-0.48	35-42	-0.44	35-42	-0.44	35-42
BB-32C	49.5	49.5	1Fe	1.11Fe	-1.07	7-14	+0.29	1-3	-0.38	21-28	-0.36	21-28	-	-
BB-33C	49	49	2Fe	2.04Fe	+0.07	3-7	+0.12	1-3	-0.31	14-21	-0.43	14-21	-	-
BB-34	50	50	1000 ppm O	959 ppm O	-0.32	42-49	-0.23	35-42	-0.23	77-84	-0.24	91-98	-0.21	98-105
BB-36	50	50	100-200 ppm O	158 ppm O	-0.13	112	-0.17	49-56	-0.17	77-84	-0.19	56-63	-0.14	77-84
BB-37	50	50	120 ppm N	180 ppm N	-0.20	63-70	-0.25	21-28	-0.21	70-77	-0.23	70-77	-0.19	77-84
BB-41	50	50	200 ppm C	200 ppm C	-0.21	56-63	-0.20	49-56	-0.22	70-77	-0.15	14-21	-0.19	105-112
BB-42	50	50	300 ppm C	340 ppm C	-0.19	84-91	-0.23	56-63	-0.20	91-98	-0.21	91-98	-0.20	>112

(a) Testing Conditions:

1 - As fabricated

2 - 1 hr, 800 C, water quenched

3 - 1 hr, 800 C, furnace cooled

4 - 1 hr, 800 C, furnace cooled, plus 14 days, 550 C, air cooled

5 - 1 hr, 800 C, furnace cooled, plus 10 per cent reduction, plus 24 hr, 550 C, air cooled, plus 10 per cent reduction for 24 hr, 550 C, air cooled.

(b) Alloys tested in the as-cast condition instead of as-fabricated condition are indicated by a "C" after the final digit of the alloy number. Aging for these was 24 hr at 580 C rather than 14 days at 550 C.

(c) All water quenching, except for alloys described in (a) above involved quenching without breaking the Vycor tube.

(d) Rate calculated when weight change became linear with time.

(e) Time to cracking, disintegration, or complete oxidation.

(f) Base alloy contained 50 ppm nitrogen and 70 ppm carbon.

(g) Rate calculated after corner cracked off at 21 days' exposure.

> - indicates that samples have not failed.

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TABLE 3. HARDNESS AND MICROSTRUCTURE DATA ON URANIUM-50 w/o ZIRCONIUM-BASE ALLOYS TESTED IN 680 F DEGASSED WATER

Microstructure and Hardness Data for Indicated Testing Condition ^(a)																
Alloy	Actual Alloy Content, w/o	Condition 1 ^(b)		Condition 2 ^(c)		Condition 3		Condition 4		Condition 5						
		Micro-structure ^(d)	VHN (10-Kg Load)		Micro-structure ^(d)	VHN (10-Kg Load)		Micro-structure ^(d)	VHN (10-Kg Load)		Micro-structure ^(d)	VHN (10-Kg Load)				
			Before	After		Before	After		Before	After		Before	After	Before	After	
BB-35 ^(e)	860 ppm O	T, A1	366	—	T, A1	357	—	T, A1	317	—	T, A1	342	—	T, A1*	236	376
BB-1	1.08Mo	T, A1	232	425	T, A1, C6	405	—	T, A1, C6	390	—	T, A1, C6	376	—	T, A1, C6	254	—
BB-2	5.11Mo	T, A1, C6	268	—	T, A1, C6	264	—	T, A1, C6	360	—	T, A1, C6	478	—	T, A1, C6	253	409
BB-3	10.2Mo	T, A1, C6	342	—	T, A1, C6	336	—	T, A1, C6	325	—	T, A1, C6	493	—	T, A1, C6*	333	—
BB-3.25C	0.27Ta	T, A1	222	—	T, A1	245	—	T, A1	238	—	T, A1	253	—	—	—	—
BB-3.5C	0.57Ta	T, A1	270	—	T, A1	224	—	T, A1	245	—	T, A1	232	—	—	—	—
BB-4	1.06Ta	T, A1	230	—	T, A1	387	—	T, A1	345	—	T, A1	383	—	T, A1*	299	—
BB-5	5.07Ta	T, A1	232	—	T, A1	376	—	T, A1	417	—	T, A1*	409	—	T, A1*	417	—
BB-6	9.8Ta	T, A1, C	230	429	T, A1, C	306	—	T, A1	429	—	T, A1*	387	—	T, A1*	287	455
BB-43C	0.077Ta 0.52Ni	T, A1	264	—	T, A1	236	—	T, A1	283	—	T, A1	245	—	—	—	—
BB-7	0.98V	T, A1	243	464	T, A1, C	459	—	T, A1	394	—	T, A1, C7	360	—	T, A1, C7	283	—
BB-8	4.92V	T, A1	264	—	T, A1	498	—	T, A1	421	—	T, A1	383	—	T, A1, C7	264	—
BB-9C	9.8V	T, A1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
BB-9C	9.8V	T, A1	345	—	T, A1	319	—	T, A1	325	—	T, A1	333	—	—	—	—
BB-10	1.0Ti	T, A1	272	—	T, A1	409	—	T, A1	336	306	T, A1	292	—	T, A1	233	—
BB-11	4.4Ti	T, A1	230	—	T, A1	433	—	T, A1	442	—	T, A1	401	—	T, A1	363	—
BB-12	10.3Ti	T, A1	238	—	T, A1	493	—	T, A1	503	—	T, A1	394	—	T, A1*	357	—
BB-13	0.69Cr	T, A1	394	—	T, A1	409	—	T, A1, C3	333	—	T, A1*	327	—	T, A1	—	—
BB-14	4.61Cr	T, A1, C3	417	—	T, A1, C3	437	—	T, A1, C3	373	—	T, A1, C3	370	—	T, A1, C3	264	—
BB-15	9.73Cr	T, A1, C3	455	—	T, A1, C3	478	—	T, A1, C3	429	—	T, A1, C3	433	397	T, A1, C3	387	—
BB-16	0.4W	T, A1, C4	274	—	T, A1, C4	413	—	T, A1	354	—	T, A1, C4	357	—	T, A1, C4	245	—
BB-17	1.05W	T, A1, C4	417	421	T, A1, C4	413	—	T, A1, C4	387	—	T, A1, C4*	351	—	T, A1, C4	216	—
BB-18	2.64W	T, A1, C4	464	—	T, A1, C4	450	—	T, A1, C4	397	—	T, A1, C4	383	—	T, A1, C4*	238	—
BB-19	0.96Al	T, A1, C5	348	—	T, A1	459	—	T, A1, C5	401	—	T, A1, C5	383	—	T, A1, C5	258	—
BB-20	1.98Al	T, A1	473	—	T, A1, C5	450	—	T, A1, C5	413	—	T, A1, C5	405	—	T, A1, C5	272	519
BB-21	4.0Al	T, A1	514	—	T, A1, C5	493	—	T, A1, C5	468	—	—	525	—	—	—	—
BB-22	0.95Sn	T, A1	373	—	T, A1	421	—	T, A1	387	—	T, A1	322	—	T, A1	228	—
BB-23	1.97Sn	T, A1, C2	401	442	T, A1, C2	405	—	T, A1, C2	373	—	T, A1, C2	330	—	T, A1, C2*	274	—
BB-24	3.82Sn	T, A1, C2	306	—	T, A1, C2	433	—	T, A1, C2	383	—	T, A1, C2	366	—	T, A1, C2	238	—
BB-25	0.5Pt	T, A1	292	—	T, A1	433	—	T, A1	325	—	T, A1	312	—	T, A1*	218	—
BB-26	0.88Pt	T, A1	468	—	T, A1	429	459	T, A1	394	—	T, A1	326	—	T, A1*	254	—
BB-27	1.93Pt	T, A1	401	—	T, A1, C	446	—	T, A1	376	—	T, A1*	366	—	T, A1	225	425
BB-28	0.53Ni	T, A1	354	—	T, A1	383	373	T, A1	299	—	T, A1	274	—	T, A1	221	—
BB-29	0.95Ni	T, A1	225	—	T, A1	351	370	T, A1	281	—	T, A1, C	272	357	T, A1	242	—
BB-30	1.94Ni	T, A1	251	405	T, A1	373	401	T, A1	304	—	T, A1	287	—	T, A1	309	—
BB-31	0.48Fe	T, A1	345	—	T, A1	360	—	T, A1	294	—	T, A1	292	—	T, A1	285	—
BB-32C	1.11Fe	T, A1	437	—	T, A1	417	—	T, A1	309	—	T, A1	330	—	—	—	—
BB-33C	2.04Fe	T, A1	437	—	T, A1	417	—	T, A1	268	—	T, A1	348	—	—	—	—
BB-34	959 ppm O	T, A1	243	—	T, A1	359	—	T, A1	314	—	T, A1	240	—	T, A1*	210	—
BB-36	158 ppm O	T, A1	302	—	T, A1	342	—	T, A1	274	—	T, A1*	274	—	T, A1*	209	—
BB-37	180 ppm N	T, A1*	297	—	T, A1	370	—	T, A1	312	—	T, A1*	306	—	T, A1*	228	—
BB-41	200 ppm C	T, A1, C1	260	—	T, A1, C1	351	—	T, A1, C1	287	—	T, A1, C	302	—	T, A1, C1*	218	—
BB-42	340 ppm C	T, C1	233	—	T, A1, C1	373	—	T, A1	289	—	—	306	—	—	225	—

(a) Testing Conditions:

1 - As fabricated

2 - 1 hr, 800 C, water quenched

3 - 1 hr, 800 C, furnace cooled

4 - 1 hr, 800 C, furnace cooled, plus 14 days, 550 C, air cooled

5 - 1 hr, 800 C, furnace cooled, plus 10 per cent reduction, plus 24 hr, 550 C, air cooled, plus 10 per cent reduction, plus 24 hr, 550 C, air cooled.

(b) Alloys tested in as-cast condition instead of as-fabricated condition are indicated by a "C" after the final digit of the alloy number. Aging for these was 24 hr at 580 C rather than 14 days at 550 C.

(c) All water quenching, except for alloys described in (b) above involved quenching without breaking the Vycor tube.

(d) Code for microstructures:

T - transformed alloy in which some epsilon has formed

A1 - alpha zirconium

A2 - alpha uranium

B - retained beta

C1 - carbide compound

C2 - tin compound

C3 - chromium compound

C4 - tungsten compound

C5 - aluminum compound

C6 - molybdenum compound

C7 - vanadium compound

* - alloy segregated.

(e) Base alloy contained 50 ppm nitrogen and 70 ppm carbon.

TABLE 4. CORROSION RESULTS OBTAINED ON URANIUM-40 w/o ZIRCONIUM-BASE ALLOYS TESTED IN 680 F DEGASSED WATER

Alloy	Corrosion Results for Indicated Testing Condition ^(a)													
	Alloy Content, w/o				Condition 1 ^(b)		Condition 2 ^(c)		Condition 3		Condition 4		Condition 5	
	Nominal		Addition		Rate ^(d) , mg/(cm ²)(hr)	Life ^(e) , days	Rate ^(d) , mg/(cm ²)(hr)	Life ^(e) , days	Rate ^(d) , mg/(cm ²)(hr)	Life ^(e) , days	Rate ^(d) , mg/(cm ²)(hr)	Life ^(e) , days	Rate ^(d) , mg/(cm ²)(hr)	Life ^(e) , days
	Uranium	Zirconium	Nominal	Actual										
CC-13 ^(f)	60	40	690 ppm O	996 ppm O	-0.29	28-35	-0.55	3-7	-0.34	35-42	-1.03	14-21	-0.51	28-35
CC-1A	57	38	5.0Mo	4.8Mo	-	0-1	-	0-1	-	0-1	-	0-1	-	0-1
CC-1B	60	35	5.0Mo	5.0Mo	-	0-1	-	0-1	Not tested		Not tested		Not tested	
CC-2A	57	38	5.0Ta	4.9Ta	-	0-1	-	0-1	-0.11	>112 ^(g)	-0.13	>112	-0.10	35-42
CC-2B	60	35	5.0Ta	4.8Ta	-	0-1	-	0-1	-0.08	>14	-0.11	>14	Not tested	
CC-3A	57	38	5.0V	4.9V	-	0-1	-	0-1	-16.3	1-3	-	0-1	-	0-1
CC-3B	60	35	5.0V	5.1V	Not tested		-	0-1	-	0-1	Not tested		Not tested	
CC-4A	57	38	5.0Ti	4.8Ti	-	0-1	-	0-1	-	0-1	-	0-1	-	0-1
CC-4B	60	35	5.0Ti	4.6Ti	-	0-1	-	0-2	-	0-1	-	0-1	Not tested	
CC-5A	57	38	5.0Cr	5.0Cr	-0.89	7-14	-0.76	7-14	-1.07	7-14	-13.2	1-3	-10.3	1-3
CC-5B	60	35	5.0Cr	4.8Cr	Not tested		Not tested		Not tested		Not tested		Not tested	
CC-6	58.8	39.2	2.0W	1.57W	-0.57	3-7	-0.56	14-21	-0.36	21-28	-1.92	7-14	-2.12	3-7
CC-7	58.8	39.2	2.0Al	1.72Al	-	0-1	-	0-1	-	0-1	-	0-1	Not tested	
CC-8	58.8	39.2	2.0Sn	2.0Sn	-	0-1	-	0-1	-1.87	7-14	-13.3	1-3	-	0-1
CC-9	59.4	39.6	1.0Pt	1.04Pt	-0.52	21-28	-0.56	1-3	-0.43	21-28	-4.24	1-3	-3.01	3-7
CC-10	59.4	39.6	1.0Ni	0.98Ni	-0.51	7-14	-0.22	7-14	-3.88	1-3	-3.37	1-3	-4.12	1-3
CC-12	60	40	1000 ppm O	890 ppm O	-1.07	1-3	-	0-1	-0.37	14-21	-2.92	7-14	-1.55	14-21
CC-14	60	40	100 ppm O	100 ppm O	-1.03	14-21	-1.02	14-21	-0.29	49-56	-1.10	7-14	-0.36	28-35
CC-15	60	40	120 ppm N	130 ppm N	-0.78	14-21	-0.62	21-28	-0.29	35-42	-1.58	3-7	-0.70	21-28
CC-16	60	40	300 ppm C	270 ppm C	-0.45	21-28	-	0-1	-0.37	14-21	-1.79	7-14	-0.58	35-42
CC-17	60	40	200 ppm C	230 ppm C	-0.52	3-7	-	0-1	-0.31	56-63	-1.18	14-21	-0.56	35-42
CC-11C	59.5	39.5	1Fe	1.05Fe	-6.13	1-3	-	0-1	-0.51	7-14	-0.93	1-3	-	-

(a) Testing Conditions:

1 - As fabricated

2 - 1 hr, 800 C, water quenched

3 - 1 hr, 800 C, furnace cooled

4 - 1 hr, 800 C, furnace cooled, plus 14 days, 550 C, air cooled

5 - 1 hr, 800 C, furnace cooled, plus 10 per cent reduction, 24 hr, 550 C, air cooled, plus 10 per cent reduction, 24 hr, 550 C, air cooled

(b) Alloys tested in the as-cast condition instead of the as-fabricated condition are indicated by a "C" after the final digit of the alloy number. Aging for these was 24 hr at 580 C rather than 14 days at 550 C.

(c) All water quenching, except for alloys described in (b) above involved quenching without breaking the Vycor tube.

(d) Rate calculated when weight change became linear with time.

(e) Time to cracking, disintegration, or complete oxidation.

(f) Base alloy contained 500 ppm nitrogen and 60 ppm carbon.

(g) > indicates that samples have not failed.

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TABLE 5. MICROSTRUCTURE AND VICKERS HARDNESS OF URANIUM-40 w/o ZIRCONIUM-BASE ALLOYS TESTED IN 680 F DEGASSED WATER

Microstructure and Hardness Data for Indicated Testing Condition ^(a)																
Alloy	Actual Alloy Content, w/o	Condition 1 ^(b)		Condition 2 ^(c)			Condition 3			Condition 4			Condition 5			
		Micro-structure ^(d)	VHN(10-Kg Load)		Micro-structure ^(d)	VHN(10-Kg Load)		Micro-structure ^(d)	VHN(10-Kg Load)		Micro-structure ^(d)	VHN(10-Kg Load)		Micro-structure ^(d)	VHN(10-Kg Load)	
			Before	After		Before	After		Before	After		Before	After		Before	After
CC-13 ^(e)	996 ppm O	—	376	366	T, A2, A1	360	—	T, A2, A1	319	—	T, A2, A1	306	—	T, A2, A1	297	—
CC-1A	4.8Mo	—	270	—	T, A2, C6	274	—	T, A2	417	—	T, A2*	536	—	T, A2*	397	—
CC-1B	5.0Mo	T, A2*	309	—	T, A2	306	—	T, A2	433	—	T, A2	566	—	T, A2	508	—
CC-2A	4.9Ta	T, A2	446	366	T, A2	394	—	T, A2	394	—	T, Aq*	322	—	—	—	348
CC-2B	4.8Ta	T, A2	238	—	T, A2	397	—	T, A1 or A2	409	—	T, A2	370	—	T, A2*	249	—
CC-3A	4.9V	—	276	—	T, A2, C7	297	—	T, A2, C7	222	—	T, A2, C	279	—	T, A2, C*	242	—
CC-3B	5.1V	T, A2, C	306	—	T, A2, C7	473	—	T, A2	417	—	T, A2	417	—	T, A2, C7	429	—
CC-4A	4.8Ti	T, A2	245	—	T, A2	421	—	T, A2	508	—	T, A2	409	—	T	376	—
CC-4B	4.6Ti	T, A2*	247	—	T, A2	421	—	T, A2	464	—	T, A2	429	—	T, A2	417	—
CC-5A	5.0Cr	T, A2, C3	274	—	T, A2, C3	425	360	T, A2, C3	354	—	T, A2, C3	314	—	T, A2, C3	380	—
CC-5B	4.8Cr	T, A2, C3	483	—	T, A2, C3	433	—	T, A2, C3	373	—	T, A2, C3	376	—	T, A2, C3	501	—
CC-6	1.57W	T, A2	233	—	T, A2	357	336	T, A2	383	—	T, A2, C4*	342	—	T, A2*	230	—
CC-7	1.72Al	T, A2	327	—	T, A2	525	—	T, A2	455	—	T, A2	478	—	T, A2	429	—
CC-8	2.0Sn	T, A2, C2	268	—	T, A2, C2	409	—	T, A2 or C2	360	—	T, A2 or C2*	345	—	T, A2, C2*	342	—
CC-9	1.04Pt	T, A2	258	—	T, A2	435	514	T, A2	357	—	T, A2*	357	—	T, A2*	348	—
CC-10	0.98Ni	T, A2, A1	357	—	T, A2, A1	370	—	T, A1	299	—	T, A1	304	—	T, A2, A1	242	—
CC-12	890 ppm O	T, A2, A1	235	387	T, A2	389	—	T, A2	317	—	T, A2, A1	312	—	T, A2, A1	260	—
CC-14	100 ppm O	T, A2	302	336	T, A2	363	—	T, A2	297	—	T, A2	232	—	T, A2	272	—
CC-15	130 ppm N	T, A2	336	380	T, A2	348	—	T, A2	327	—	T, A2, A1	312	—	T, A2	228	—
CC-16	270 ppm C	T, A2, C1	285	336	T, A2, C1	405	—	B, C1	319	—	T, A2, C1	287	—	T, A2 or C1*	262	357
CC-17	230 ppm C	T, C1	236	—	T, A2, C1	421	—	T, A2, C1	333	—	T, A2, C1	309	—	T, A2 or C1	258	—
CC-11C	1.05Fe	T, A2	272	—	T, A2*	397	—	T, A2	366	—	T, A2	351	—	—	—	—

(a) Testing Conditions

1 - As fabricated

2 - 1 hr, 800 C, water quenched

3 - 1 hr, 800 C, furnace cooled

4 - 1 hr, 800 C, furnace cooled, plus 14 days, 550 C, air cooled

5 - 1 hr, 800 C, furnace cooled, plus 10 per cent reduction, 24 hr, 550 C, air cooled, plus 10 per cent reduction, 24 hr, 550 C, air cooled.

(b) Alloys tested in the as-cast condition instead of as-fabricated condition are indicated by a "C" after the final digit of the alloy number. Aging for these was 24 hr at 580 C rather than 14 days at 550 C.

(c) All water quenching, except for alloys described in (a) above involved quenching without breaking the Vycor tube.

(d) Code for microstructures.

T - transformed alloy in which some epsilon has formed

A1 - alpha zirconium

A2 - alpha uranium

B - retained beta

C1 - carbide compound

C2 - tin compound

C3 - chromium compound

C4 - tungsten compound

C5 - aluminum compound

C6 - molybdenum compound

C7 - vanadium compound

* - alloy segregated.

(e) Base alloy contained 50 ppm nitrogen and 60 ppm carbon.

Corrosion Behavior

Uranium-50 w/o Zirconium Alloys

Studies of the corrosion behavior in 680 F water of the uranium-50 w/o zirconium alloy with and without ternary additions indicate that the oxide film formed during corrosion was not protective, and, in general, alloy samples lost weight at a constant rate after 7 to 14 days of initial exposure. Exceptions were the as-fabricated and the beta-quenched nickel alloys and the beta-furnace-cooled 1 and 2 w/o platinum alloys. Adherent films formed on these samples resulted in a weight gain for the majority of the test. However, the samples began to lose weight one or two exposure periods (7 to 14 days) before cracking or distintegration. As illustrated in Figure 1, the adherent oxide film formed at a linear rate and did not protect the underlying metal.

The binary uranium-50 w/o zirconium alloy corroded at a rate of about $-0.20 \text{ mg}/(\text{cm}^2)(\text{hr})$ regardless of the heat treatment, and had a maximum corrosion life of about 100 days (this rate is about four times greater than for a similar alloy tested in 600 F water).⁽³⁾ However, rapid cooling from the beta field resulted in shorter corrosion life. The binary alloy contained 860 ppm oxygen, 70 ppm carbon, and 47 ppm nitrogen. No marked effect on corrosion behavior was noted when oxygen content was varied between 158 and 959 ppm, when carbon was raised to 340 ppm, or when nitrogen was raised to 180 ppm.

Of the ternary additions studied, only tantalum resulted in improved corrosion resistance. As little as 1 w/o addition halved the corrosion rate, reducing it to $-0.10 \text{ mg}/(\text{cm}^2)(\text{hr})$ and resulted in prolonged corrosion life. At 5 w/o tantalum, the rate was further reduced to around $-0.06 \text{ mg}/(\text{cm}^2)(\text{hr})$. The 10 w/o tantalum alloy also exhibited low corrosion rates, but its corrosion life was much shorter in the beta-quenched and warm-worked conditions than similarly treated binaries. The effect of tantalum on lowering corrosion rate and prolonging corrosion life is shown in Figure 2.

Several ternary additions had essentially no effect on corrosion life of the binary alloys. Ternary additions and the particular heat treatments which exhibited this behavior are listed below:

- 1 w/o molybdenum - as fabricated
- 1 w/o chromium - aged 14 days at 550 C
- 0.5, 1, 2 w/o platinum - as fabricated
- 0.5, 2 w/o platinum - beta quenched
- 0.5 w/o iron - beta quenched.

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FIGURE 1. THE CORROSION BEHAVIOR OF URANIUM-50 w/o ZIRCONIUM ALLOYS CONTAINING NICKEL ADDITIONS IN 680 F DEGASSED WATER

Samples as fabricated.

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FIGURE 2. EFFECT OF TANTALUM ADDITIONS ON THE CORROSION BEHAVIOR OF URANIUM-50 w/o ZIRCONIUM ALLOYS IN 680 F DEGASSED WATER

Samples as fabricated.

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All other heat treatments of the above-listed alloys exhibited poorer corrosion behavior than the binary alloy similarly treated.

The following alloys were less resistant than the binary alloy in all heat-treated conditions studied:

- 5, 10 w/o chromium or molybdenum
- 1, 5, 10 w/o titanium
- 1, 5 w/o vanadium
- 1, 2, 4 w/o aluminum, tin, or tungsten
- 0.5, 1, 2 w/o nickel.

Aluminum, titanium, vanadium, and the 5 and 10 w/o molybdenum additions to the binary alloy resulted in very rapid failure, with most samples cracking or disintegrating within a 3-day exposure.

The following uranium-50 w/o zirconium-base alloys were corrosion tested in the as-cast and heat-treated conditions:

- 1, 2 w/o iron (not fabricable)
- 10 w/o vanadium (not fabricable)
- 0.2, 0.5 w/o tantalum
- 0.07 w/o tantalum* plus 0.5 w/o nickel.

Corrosion results for these alloys are given in Tables 2 and 3. These alloys were sensitive to heat treatment and exhibited maximum corrosion life in the furnace-cooled and in the aged conditions. The ternaries containing tantalum were the most resistant with the rate of $-0.15 \text{ mg}/(\text{cm}^2)(\text{hr})$ for the 0.2 w/o tantalum alloy. Increasing the tantalum to 0.5 w/o decreased the corrosion rate to $-0.13 \text{ mg}/(\text{cm}^2)(\text{hr})$, which approached that of the 1 w/o tantalum alloy. Figure 3 contains a plot of the corrosion rates of furnace-cooled uranium-50 w/o zirconium alloys as a function of tantalum content. The theoretical life, assuming linear corrosion of specimens, has been calculated and is also plotted in Figure 3 as a dotted line. The alloy with a tantalum content at the level of 10 w/o, however, exhibited discontinuous failure and deviated considerably from its theoretical life. Up to about 5 w/o tantalum the theoretical life should be a fair engineering approximation. The alloy containing 0.5 w/o nickel and 0.07 w/o tantalum resulted in the formation of an adherent oxide film, but the corrosion life was also shortened. The addition of 1 or 2 w/o iron to the uranium 50 w/o zirconium alloy resulted in short corrosion life, while the ternary alloy containing 10 w/o vanadium completely disintegrated within 24 hr for all heat treatments.

*It was intended to add the 0.5 w/o nickel to a uranium-50 w/o zirconium-0.5 w/o tantalum base, but the tantalum was apparently lost during melting, with the result of a 0.07 w/o tantalum level.

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FIGURE 3. EFFECT OF TANTALUM ADDITIONS ON THE CORROSION RATE OF URANIUM-50 w/o ZIRCONIUM-BASE ALLOYS IN 680 F WATER

All specimens furnace cooled from the beta field.

Uranium-40 w/o Zirconium Alloys

Like the uranium-50 w/o zirconium alloys, the oxide film formed on the uranium-40 w/o zirconium alloys was not protective, and, in general, the alloy samples lost weight at a constant rate. As expected, the uranium-40 w/o zirconium alloys corrosion tested in 680 F water were inferior to the uranium-50 w/o zirconium alloys. No adherent films were observed on any of the uranium-40 w/o zirconium alloys, and, as indicated in Tables 4 and 5, many of them had high corrosion rates with short life. The uranium-40 w/o zirconium alloys tested are indicated below:

100, 632, 890, 996 ppm oxygen
50, 230, 270 ppm carbon
30, 50, 130 ppm nitrogen
1 w/o nickel, platinum, or iron
2 w/o aluminum, tin, or tungsten
5 w/o chromium, molybdenum, tantalum, titanium,
or vanadium.

In general, the alloys exhibited maximum corrosion resistance when furnace cooled from the beta field or when warm worked at 425 C and annealed at 550 C. Maximum corrosion resistance of the binary alloy was in the beta-furnace-cooled condition, with a life of 35 to 42 days and a corrosion rate of $-0.34 \text{ mg}/(\text{cm}^2)(\text{hr})$. Lowering the oxygen content to 100 ppm*, increasing the carbon up to 300 ppm, or increasing nitrogen up to 120 ppm did not appear to affect the corrosion rate of the base alloy.

Of the ternary alloys evaluated, only the alloy containing 5 w/o tantalum appeared promising. This alloy was most resistant in the furnace-cooled and in the aged conditions. Corrosion rates for this alloy were as low as -0.11 to $-0.13 \text{ mg}/(\text{cm}^2)(\text{hr})$, which is approximately one-third that of the most resistant base alloy. Corrosion life was in excess of 112 days — more than twice that of the base alloy. A comparison of the corrosion behavior of the 5 w/o tantalum alloy with the uranium-40 w/o zirconium base is shown in Figure 4.

Alloys containing the following ternary additions were not resistant in any of the heat-treated conditions studied:

1 w/o nickel, platinum, or iron
2 w/o aluminum, tin, or tungsten
5 w/o chromium, molybdenum, titanium, or vanadium.

*The two alloys, CC-12 and CC-13 (see Tables 4 and 5), contained about the same amount of oxygen apparently due to arc-melting difficulties. The alloy with the higher oxygen content showed better corrosion resistance.

FIGURE 4. EFFECT OF TANTALUM ADDITIONS ON THE CORROSION BEHAVIOR OF URANIUM-40 w/o ZIRCONIUM ALLOYS IN 680 F DEGASSED WATER

Most of these alloys exhibited very poor resistance and cracked or disintegrated within a 3-day exposure.

The 1 w/o iron alloy which was not fabricable was tested in the as-cast and some heat-treated conditions, and in all cases had a short corrosion life.

Hardness and Microstructure

Data for hardness and microstructure also are presented in Tables 2, 3, 4, and 5. Hardnesses for the water-quenched conditions refer, not to a true water quench, but to some intermediate cooling rate, because the Vycor tubes were not broken upon quenching. The binary uranium-50 w/o zirconium alloy (BB-35) in this condition has a hardness of 357 VHN as compared to a value of approximately 306 VHN for a true water-quenched specimen. This value (306 VHN) is somewhat higher than hardness values of about 230 VHN found by Chubb⁽⁴⁾ in water-quenched binary alloys of similar compositions. The hardness of 357 VHN corresponds approximately to the peak aging condition for the base alloy and also the poorest resistance to corrosion in 680 F water. For all the other three heat-treated conditions of the uranium-50 w/o zirconium base, the hardness dropped in every case corresponding to overaging. The associated corrosion life increased about 50 per cent.

Hardness and microstructure in general cannot be correlated with corrosion resistance. For instance, tantalum additions to both the base alloys in most heat-treated conditions improve the corrosion behavior considerably in 680 F water, but the associated microconstituents appear to be almost identical to those in the base alloys (see Figures 5 and 6, for example). The hardnesses of the improved alloys containing tantalum were sometimes greater and sometimes less than the corresponding binary bases.

The microstructural differences which were observed in the alloys may be grouped into two categories: those exhibiting a finer or coarser structure than found in the binary; and those which contained a third phase. The nickel additions give a relatively coarse microstructure (Figure 7), which predominated in all heat treatments. It is not clear whether or not the coarse structure is important in regard to the low corrosion rates and short life that nickel seems to promote. Third phases (Figure 8), assumed to be compounds, were observed in ternary alloys containing aluminum, chromium, molybdenum, platinum, tin, tungsten, and vanadium. All of these, except the as-fabricated 1 w/o molybdenum alloy, had poorer resistance to corrosion than the binary alloy, and it may be tentatively concluded that third phases in the form of compounds are detrimental to corrosion resistance in 680 F water.

FIGURE 5. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM BASE
FURNACE COOLED FROM 800 C

Structure consists of alpha zirconium and epsilon matrix.

FIGURE 6. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM-BASE
WITH 10 w/o TANTALUM ADDITION

Same heat treatment as in Figure 4.

FIGURE 7. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM BASE
WITH 2 w/o NICKEL ADDITION

Furnace cooled from 800 C. Coarse alpha zirconium in
epsilon matrix.

FIGURE 8. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM BASE
WITH 10 w/o CHROMIUM ADDITION

Water quenched from 800 C without breaking Vycor tube.
Abundant chromium compound (light) with some alpha
zirconium (dark) in epsilon matrix.

Oxygen and nitrogen appeared to promote transformation of the beta phase, since alpha zirconium starts to appear and also coarsens with about 900 ppm oxygen or 130 ppm nitrogen in the uranium-40 w/o zirconium base. No consistent correlations were found between the microstructures of the interstitial alloys and corrosion behavior for either the uranium-50 w/o zirconium or the uranium-40 w/o zirconium base.

Figures 9 through 11 show some of the microstructures of the base uranium-40 w/o zirconium alloys. The subgrain structure which is seen quite clearly in Figure 9 is associated with beta transformation to epsilon and alpha⁽⁵⁾. The subgrains appeared in the matrix of almost all of the alloys tested in this program.

Electrical-Resistance Changes During Aging

The aging response of a few selected specimens was studied, using changes in electrical resistance and hardness with time. The data obtained in this study are given in Table 6 and shown graphically in Figure 12. The reference condition was the beta-quenched condition in which the Vycor tubes were broken upon quenching. In Figure 12, there is a set of values marked with an asterisk. These values were obtained after beta quenching without breaking the Vycor tube, indicating that, under this condition, a cooling rate is obtained which is equivalent to aging for about 10 min. The data plotted in Figure 12 show that 10 w/o tantalum added to a uranium-50 w/o zirconium

TABLE 6. CHANGE IN ELECTRICAL RESISTANCE AND HARDNESS^(b) UPON AGING BETA-QUENCHED SPECIMENS

Base Alloy	Nominal Addition, w/o	Per Cent Change in Electrical Resistance						
		As Quenched ^(a)	After Aging at 580 C for Indicated Time					
			10 Min	30 Min	60 Min	10 Hr	24 Hr	10 Days
U-50 w/o Zr	Binary	0 (306)	31.7 (409)	30.4 (327)	29.6 (330)	26.6 (302)	27.6 (292)	25.8 (279)
U-50 w/o Zr	1Ta	0 (203)	34.7 (437)	34.2 (380)	33.5 (366)	30.6 (339)	30.3 (336)	32.1 (302)
U-50 w/o Zr	10Ta	0 (210)	5.94 (306)	6.16 (287)	4.31 (219)	13.8 (251)	21.4 (383)	26.8 (345)
U-50 w/o Zr	0.5Ni	0 (227)	34.9 (376)	34.7 (342)	33.7 (336)	32.8 (317)	32.1 (306)	34.3 (287)
U-40 w/o Zr	300 ppm C	0 (206)	27.3 (380)	26.7 (336)	25.4 (325)	18.2 (306)	18.7 (256)	17.0 (304)

(a) The Vycor tube was broken upon water quenching after 1 hr at 800 C.

(b) Vickers hardness numbers given in parentheses.

500X RM3767
FIGURE 9. MICROSTRUCTURE OF URANIUM-40 w/o ZIRCONIUM BASE
FURNACE COOLED FROM 800 C

Isolated phase is alpha zirconium in epsilon matrix. Possibly
alpha uranium precipitated in subgrain boundaries.

500X RM3986
FIGURE 10. MICROSTRUCTURE OF URANIUM-40 w/o ZIRCONIUM BASE
FURNACE COOLED FROM 800 C AND AGED 14 DAYS AT
550 C

Same as Figure 8 above except lighter etch does not show sub-
grains. Acicular alpha uranium has precipitated.

500X

RM4551

FIGURE 11. MICROSTRUCTURE OF URANIUM-40 w/o ZIRCONIUM BASE
WITH 5 w/o CHROMIUM ADDITION

Furnace cooled from 800 C. Dark grain-boundary phase of
alpha uranium. Light isolated phases are alpha zirconium
and chromium compound. Light matrix is epsilon.

FIGURE 12. CHANGE IN ELECTRICAL RESISTANCE AND HARDNESS OF SELECT ALLOYS WITH AGING TIME AT 580 C

Alloys originally water quenched from 800 C (breaking Vycor tube).

base results in a markedly different aging response, when compared with that of the other alloys tested. Referring to the corrosion behavior of the 10 w/o tantalum alloy in the beta-quenched condition (see Tables 2 and 3), the short corrosion life may be related to its lack of stability associated with a partially transformed structure. The 1 w/o tantalum alloy ages rapidly and may be considered more stable than the 10 w/o tantalum alloy after 10 days of aging at 580 C. This may account for the good corrosion resistance of the 1 w/o tantalum alloy in all heat-treated conditions. The 0.5 w/o nickel alloy ages in almost the same manner as the 1 w/o tantalum alloy, but tends to disintegrate early in corrosion tests. In fact, the 1 w/o tantalum, 10 w/o tantalum, and the 0.5 w/o nickel alloys all exhibited low corrosion rates. However, the 0.5 w/o nickel alloy had low corrosion life in all heat-treated conditions in contradistinction to the 1 w/o tantalum alloy.

As indicated in Figures 13 through 18, microstructural changes occurred during aging. Figures 13 and 14 show the aging effects in the uranium-50 w/o zirconium binary. For the nickel alloy (Figures 15 and 16), there was no apparent precipitation in the matrix during aging, although there was spheroidization of the massive phase. Figures 17 and 18 illustrate the precipitate formed upon aging a uranium-40 w/o zirconium alloy.

Corrosion Mechanism

The types of corrosion failure may be classified according to rate of oxidation, either high or low. As would be expected, alloys with high corrosion rates failed in a short time because of complete oxidation of the samples, e. g., most of the uranium-40 w/o zirconium alloys, and the aluminum, tin, titanium, and vanadium uranium-50 w/o zirconium alloys. With low corrosion rates, corrosion life would be expected to be dependent upon specimen thickness*, but this is not always the case. For instance, some specimens with low corrosion rates fail discontinuously (cracking or catastrophic oxidation) after an abnormally short time. Some of the alloys with low corrosion rates are listed below according to the type of failure:

Uniformly Corroded

Epsilonized

Uranium-50 w/o zirconium base
Uranium-40 w/o zirconium base
Uranium-40 w/o zirconium plus 5 w/o tantalum

*A maximum corrosion life of about 100 days was obtained in the epsilon condition. This life corresponded roughly with the time required for complete oxidation at the rate of $-0.2 \text{ mg}/(\text{cm}^2)(\text{hr})$. According to this, longer life can be expected with thicker specimens.

500X

N29199

FIGURE 13. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM BASE
WATER QUENCHED FROM 800 C

No aging. Vycor capsule broken upon quenching.

500X

N29188

FIGURE 14. SAME ALLOY AS IN FIGURE 13 ABOVE AFTER
AGING 24 HR AT 580 C

Some evidence of precipitation of alpha zirconium.

FIGURE 15. MICROSTRUCTURE OF URANIUM-50 w/o ZIRCONIUM BASE CONTAINING 0.5 w/o NICKEL AFTER WATER QUENCHING FROM 800 C

No aging. Vycor capsule broken upon quenching.

FIGURE 16. SAME ALLOY AS IN FIGURE 15 ABOVE AFTER AGING 240 HR AT 580 C

Spherodization of the alpha-zirconium phase appears to be the only effect of aging.

500X

N29191

FIGURE 17. MICROSTRUCTURE OF URANIUM-40 w/o ZIRCONIUM BASE
CONTAINING 300 PPM CARBON AFTER WATER QUENCHING
FROM 800 C

No aging. Vycor tube broken upon quenching.

500X

N29185

FIGURE 18. SAME ALLOY AS IN FIGURE 17 ABOVE AFTER AGING
FOR 24 HR AT 580 C

Alpha-uranium precipitate now visible.

Uniformly Corroded (continued)

All heat treatments	Uranium-50 w/o zirconium plus 1 or 5 w/o tantalum
As fabricated	Uranium-50 w/o zirconium plus 0.5, 1, or 2 w/o platinum

Discontinuous Failure

All heat treatments	Uranium-50 w/o zirconium plus 0.5, 1, or 2 w/o nickel Uranium-50 w/o zirconium plus 5 or 10 w/o molybdenum Uranium-50 w/o zirconium plus 0.5, 1, or 2 w/o tungsten Uranium-50 w/o zirconium plus 0.5 w/o iron
Epsilonized	Uranium-50 w/o zirconium plus 0.5, 1, or 2 w/o platinum

Because many of the specimens completely disintegrated or oxidized throughout, only a limited number of specimens were available for metallographic study after corrosion testing. From the available metallographic evidence, it appears that precipitates, which may be new phases, are associated with corrosion. This is clearly shown in the photomicrograph of the uranium-40 w/o zirconium binary alloy in Figure 19. Here, an unidentified dark-etching precipitate has formed during corrosion, which appears to be the step preceding the formation of the grayish oxide phase. After the oxide forms, stresses may then be relieved by cracking at the oxide-metal interface and further oxidation and disintegration of the specimen can occur.

A dark-etching precipitate was also observed in the uranium-50 w/o zirconium binary alloy after corrosion testing, as indicated in Figure 20 for the as-fabricated condition. This view of the specimen represents rather late stages of corrosion but does show the numerous veins of dark precipitate probably following a stress-relieving pattern. The precipitate here may be following subgrain boundaries, but, because of the fineness of the structure, this cannot be stated without reservation. Since the subgrains are slightly out of register with each other regarding lattice orientation, the subgrain boundaries should be more active chemically than the interior of the grains.

It is well known that stress-corrosion cracking may follow paths dependent upon a precipitate where the precipitate forms as a result of previous thermal history or forms in situ as a result of high-stress conditions at the base of a crack. Both of these mechanisms were observed here.

500X

N29186

FIGURE 19. MICROSTRUCTURE OF URANIUM-40 w/o ZIRCONIUM BASE AFTER CORROSION TESTING IN 680 F WATER

Specimen originally furnace cooled from 800 C. Note the dark precipitate along the prior-beta grain boundary with the gray oxide finger contained therein.

500X

N29198

FIGURE 20. MICROSTRUCTURE OF THE AS-FABRICATED URANIUM-50 w/o ZIRCONIUM BASE AFTER CORROSION TESTING IN 680 F WATER

Dark mass of corrosion product in upper right quadrant. Note also the relatively fine fingers of precipitate extending from the mass into the metallic base.

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SUMMARY

- (1) The uranium-50 w/o zirconium base corroded at the rate of approximately $-0.20 \text{ mg}/(\text{cm}^2)(\text{hr})$ in 680 F water. No marked effect on corrosion behavior was noted when oxygen content was varied between 158 and 959 ppm, when carbon was raised from 70 to 340 ppm, or with nitrogen in the range of 47 to 180 ppm.
- (2) Tantalum additions of 1 and 5 w/o to uranium-50 w/o zirconium alloys promote excellent corrosion resistance for these alloys in all heat-treated conditions investigated. The associated corrosion rates were -0.05 to $-0.10 \text{ mg}/(\text{cm}^2)(\text{hr})$ and corrosion lives were in excess of 112 to 154 days.
- (3) Ternary additions of the following elements to uranium-50 w/o zirconium alloys, in general, lowered the corrosion resistance:
 - 1, 5, 10 w/o chromium, molybdenum, titanium
 - 1, 5, 10* w/o vanadium
 - 1, 2, 4 w/o aluminum, platinum, tungsten
 - 0.5, 1, 2 w/o nickel, platinum
 - 0.5, 1*, 2* w/o iron.
- (4) The binary uranium-40 w/o zirconium alloy was most resistant in the furnace-cooled condition with a corrosion rate of $-0.34 \text{ mg}/(\text{cm}^2)(\text{hr})$ and a life of 35 to 42 days. Lowering the oxygen from 996 to 100 ppm, increasing the carbon from 60 to 270 ppm, or increasing the nitrogen from 30 to 130 ppm did not appear to affect the corrosion behavior of the binary. In the attempt to increase oxygen above the base level of 996 ppm, an alloy was obtained which showed inferior corrosion resistance in spite of the fact that this alloy analyzed less in oxygen (890 ppm) than the base.
- (5) The only uranium-40 w/o zirconium alloys which were more resistant than the base were a furnace-cooled and an aged 5 w/o tantalum alloy. These specimens corroded at a rate of $-0.11 \text{ mg}/(\text{cm}^2)(\text{hr})$ with a life in excess of 112 days.

*Tested only in as-cast and as-cast-plus-heat-treated conditions.

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- (6) The following ternary additions to the uranium-40 w/o zirconium base lowered the corrosion resistance:

1 w/o nickel, platinum, iron*
2 w/o aluminum, tin, tungsten
5 w/o chromium, molybdenum,
tantalum**, titanium, vanadium.

- (7) In general, the uranium-40 w/o zirconium alloys exhibited maximum corrosion resistance in the epsilonized conditions***.
- (8) Except for the uranium-50 w/o zirconium alloy with 1 w/o molybdenum in the as-fabricated condition, additions of aluminum, chromium, molybdenum, platinum, tin, tungsten, and vanadium were found to decrease corrosion resistance of both the 50 w/o and 60 w/o uranium alloys. This effect is believed to be associated with the presence of a third phase, probably a compound.
- (9) No consistent correlation was found between hardness, microstructure (before corrosion tests), and corrosion behavior.
- (10) Resistance measurements offer a sensitive method of following aging behavior, but the limited results here cannot be unambiguously related to corrosion resistance.

REFERENCES

- (1) "An Evaluation of Data on Zirconium-Uranium Alloys", BMI-1030, p 83.
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- (3) Pray, H. A., and Berry, W. E., "Corrosion of Uranium Alloys in High Temperature Water", BMI-874 (October 5, 1953).
- (4) "An Evaluation of Data on Zirconium-Uranium Alloys", BMI-1030, p 37.
- (5) Chubb, Walston, Private Communication, Battelle Memorial Institute.

JER:WEB:HRO:RSP:RIJ/nlh

*Tested only in as-cast and as-cast-plus-heat-treated conditions.

**Except in the heat-treated conditions described in (5).

***Furnace cooled from the beta with or without subsequent working and annealing in the epsilon range.

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