NASA CONTRACTOR REPORT

NASA CR-1811

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CORROSION RESISTANCE OF TANTALUM, T-111, AND Cb-1Zr TO MERCURY AT 1200° F

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1971

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA CR-1811		
4. Title and Subtitle CORROSION RESISTANCE OF TANTALUM, T-111, AND Cb-1Zr TO MERCURY AT 1200° F		5. Report Date May 1971 6. Performing Organization Code
7. Author(s) L. B. Engel, Jr., and R. W. Harrison		8. Performing Organization Report No. GESP-199
9. Performing Organization Name and Address General Electric Company Cincinnati, Ohio 45215		10. Work Unit No. 11. Contract or Grant No. NAS 3-10610
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Contractor Report 14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

Sheet specimens of tantalum, T-111, and Cb-1Zr were strained 5 and 20 percent by bending. Specimens representative of each strain level, and in the as-bent and the as-bent and annealed conditions, were tested at 1200° F for 1000 hours in sealed tantalum capsules containing liquid mercury. No changes were observed in any of the specimens as a result of the exposure to mercury.

17. Key Words (Suggested by Author(s))	18. Distribution Statement		
Mercury corrosion Refractory metals	Unclassified - unlimited		
19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	25	$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

FOREWORD

The research described in this report was conducted by the General Electric Company under NASA contract NAS 3-10610. Mr. Phillip L. Stone of the Lewis Research Center Materials and Structures Division was the NASA Project Manager. The report was originally issued as General Electric report GESP-199.

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I. INTRODUCTION

The general configuration of the present SNAP-8 boiler design is seven tubes coiled in an outer shell in a tube-in-tube arrangement. The salient design feature is the use of double tube construction with unalloyed tantalum in contact with the mercury, and stainless steel in contact with the primary loop NaK. The spaces between the tubes and headers is filled with static NaK as an intermediate fluid.

The potential desire to use materials with higher strengths and greater corrosion resistance to NaK than the unalloyed tantalum presently utilized in the SNAP-8 boiler indicates the need to consider the use of refractory metal alloys. Two alloys which offer higher strength, greater corrosion resistance to NaK, and are readily available are Cb-1Zr and T-111 (Ta-8W-2Hf). The main deterrent to employment of these materials is the uncertainty of their corrosion resistance to mercury. Weeks[(1)] recently reported cracks in strained Cb-1Zr alloy specimens exposed to mercury for 168 hours at 1110, 1250, and 1380°F which he attributed to leaching of zirconium from the matrix by the mercury. He reported similar results for strained T-111 alloy after exposures at 1200 and 1380°F, and attributed this behavior to the zirconium present in the alloy as an impurity. Weeks also reported that the annealing of strained Cb-1Zr alloy specimens prior to exposing them to mercury resulted in no cracking during the exposure to mercury.

This report covers work done to further delineate the corrosion resistance of Cb-1Zr and T-111 alloys in the strained, and strained and annealed conditions to liquid mercury at 1200°F for periods of 1000 hours.

[(1)] Weeks, J.R., "Liquidus Curves and Corrosion of Fe, Cr, Ni, Co, V, Cb, Ta, Ti, Zr in 500-750°C Mercury." Corrosion, Vol. 23, No. 4, pp. 98-106, April (1967).

II. SUMMARY

Sheet specimens of tantalum, T-111 alloy, and Cb-1Zr alloy were strained 5 and 20 percent by bending. A portion of the bent test specimens was retained in the as-bent condition while portions of the remaining specimens were given selected postbend vacuum anneals. The annealing conditions selected were: 8 hours at 1600°F, 2 hours at 1900°F, and 2 hours at 2200°F. Specimens of each strain level and in the as-bent, and as-bent and annealed conditions were tested in liquid mercury at 1200°F for 1000 hours. The specimens and mercury were contained in sealed tantalum capsules. Following test, the specimens were cleane of mercury by vacuum distillation and subsequently evaluated for changes in weight, surface integrity, and metallographic structure. No changes were observed in any of the specimens as a result of the exposure to liquid mercury. Failure to observe any cracking in the as-bent Cb-1Zr and T-111 alloy specimens exposed to mercury is in direct contrast to the previously discussed results reported by Weeks[1].

III. TEST SPECIMEN PREPARATION

The test specimens were prepared from 0.040-inch-thick unalloyed tantalum, T-111 alloy (Ta-8W-2Hf), and Cb-1Zr alloy sheet. The tantalum and T-111 alloy sheets were obtained from the Norton Company, Metals Division and the Wah Chang Corporation, respectively. The chemical analyses, mechanical property, and metallographic data supplied by the vendors and obtained at G.E. - NSP on the test specimen materials as part of the quality assurance testing are given in Appendix A. A final product chemistry for the Cb-1Zr alloy sheet is also given in Appendix A. The 0.040-inch-thick sheets were sheared into 0.5-inch-wide x 1.0-inch-long test specimens. Following acid cleaning to remove surface contamination, half of the specimens for each alloy were bent using a 0.406-inch-radius ram and a 120° anvil, and the remainder of the specimens were bent with a 0.109-inch-radius ram and a 120° anvil to produce the two desired maximum strain levels in the specimens of approximately 5 and 20 percent, respectively, Figure 1. A 5 percent strain is the maximum normally incurred in bending of tubing for boiler construction.

A portion of the bent test specimens was retained in the as-bent condition while portions of the remaining specimens were given the selected postbend vacuum anneals. The annealing conditions selected were; 8 hours at 1600°F, 2 hours at 1900°F, and 2 hours at 2200°F. The 2200°F heat treatment corresponds to a typical postweld anneal for the refractory metal alloys. It is not feasible to consider vacuum annealing a composite stainless steel - refractory metal alloy boiler at temperatures above 2000°F for numerous reasons, including differential

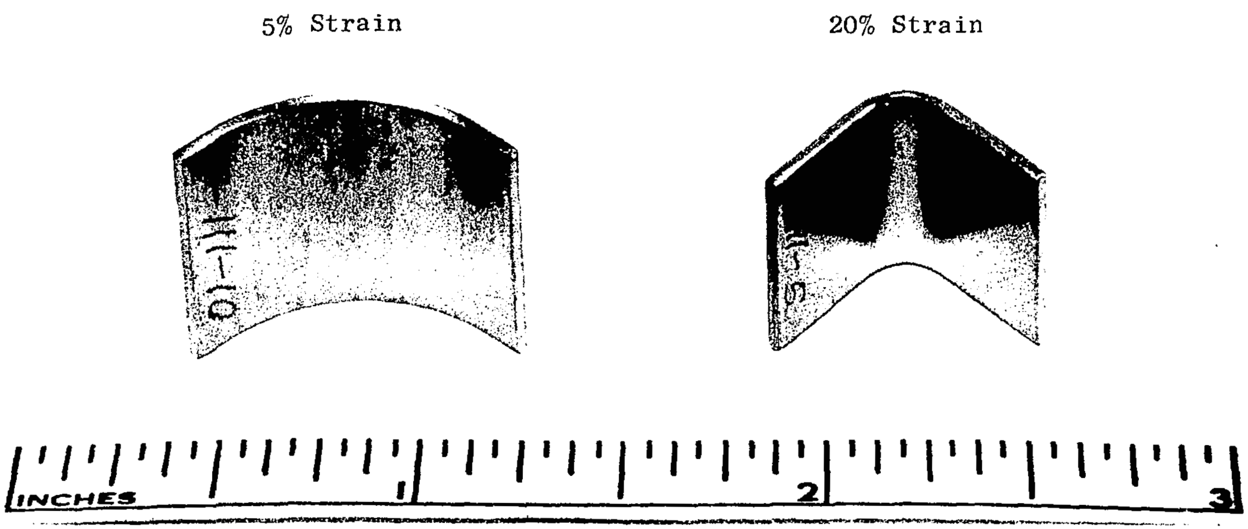


Figure 1. T-111 Alloy Specimens Before Exposure to 1200^{o}F Mercury. (Orig. C68011553)

thermal expansion difficulties and the vaporization of the stainless steel. The 1600°F heat treatment is more representative of a heat treatment which could be considered for a bimetallic boiler. The 1900°F heat treatment was selected to evaluate the effect of heat treatment in the intermediate temperature range. Subsequently, the specimens of each alloy and condition were weighed and fixtured together with tantalum wire as illustrated in Figure 2. A single test specimen assembly contained a total of eight test specimens all of the same alloy.

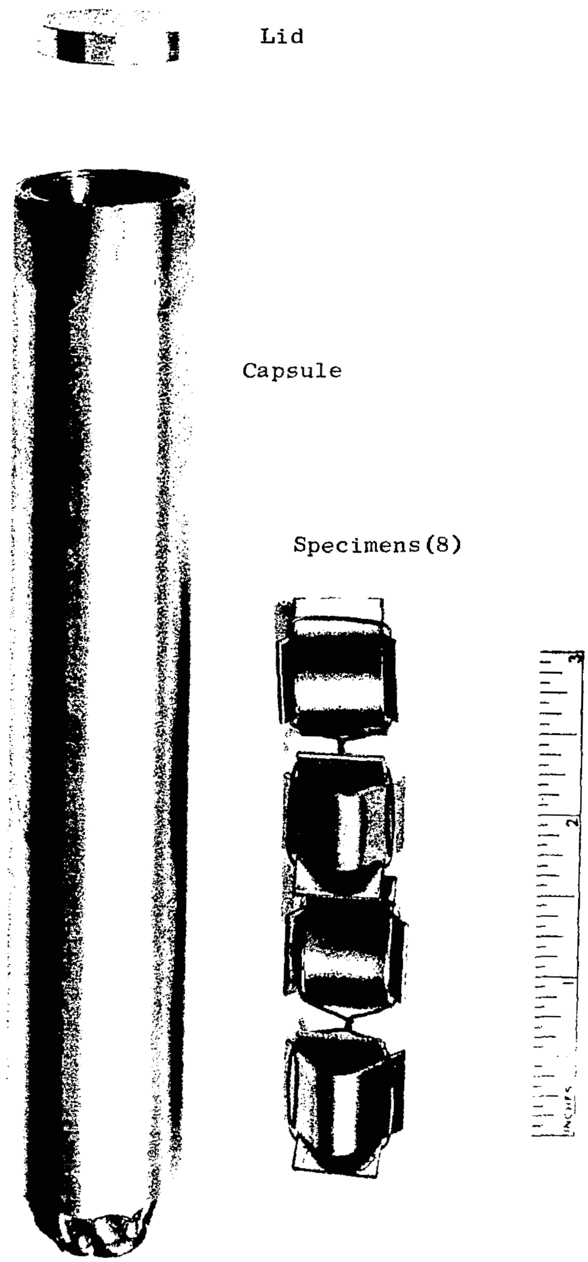


Figure 2. Tantalum Capsule and Specimens Before Assembly and Filling with Mercury. (C68011556)

IV. CAPSULE PREPARATION

Tantalum capsules were used to contain the test specimens and mercury during testing. The capsules were made from 1.0-inch-OD x 0.100-inch-thick wall seamless tantalum tubing and were six inches in length. The tubing was obtained from the Norton Company, Metals Division, and the quality assurance data supplied by the vendor and obtained at G.E. - NSP are given in Appendix A. After TIG welding the tantalum bottom cap onto the tantalum tube, Figure 2, the specimen bundle was placed inside the capsule, and the top tantalum cap TIG welded into place. A 0.0625-inch-diameter hole located in the top cap was utilized as a filling port during the loading of mercury into the capsules.

V. CAPSULE FILLING

The filling of the capsules with mercury and their subsequent sealing was accomplished in a vacuum-purged, helium-filled, TIG welding chamber. Twenty-two cubic centimeters of mercury were put into each capsule through the 0.0625-inch-diameter hole located in the top cap of each capsule. This quantity of mercury was sufficient to completely cover the test specimens with liquid mercury at the test temperature (1200°F). The spectrographic analysis of the mercury used to fill the capsules is given in Table I. The small fill holes in the tantalum capsules were then sealed by TIG welding. Copper chill blocks were used on the capsule to reduce heating of the mercury during welding, and no vaporization of mercury was observed. Since the tantalum capsules were to be tested in an air environment furnace, each capsule was placed inside a stainless steel capsule and sealed under helium in the same manner as that used for sealing the original tantalum capsules.

TABLE I.

SPECTROGRAPHIC ANALYSES OF MERCURY[(a)] USED TO FILL THE TANTALUM CAPSULES

Element	Concentration, ppm
Ta	ND[(b)]
W	ND
Cb	ND
Zr	ND
Ag	ND
Al	< 5
As	ND
B	ND
Ba	ND
Bi	ND
Ca	< 1
Cd	ND
Co	ND
Cr	< 5
Cu	< 5
Fe	< 5
K	ND
Li	ND
Mg	< 5
Mn	ND
Mo	ND
Na	ND
Ni	< 5
Pb	ND
Sb	ND
Si	< 5
Sn	ND
Sr	ND
Ti	ND
V	ND
Zn	ND

(a) Bethlehem Apparatus Company, Hellerstown, Pa.
Triple Vacuum Distilled.

(b) ND - not detected

VI. TESTING

The capsules were isothermally tested at 1200°F for 1000 hours in the air environment furnace facility shown in Figure 3. Each capsule was heated by a 1340-watt, wound nichrome resistance element which is controlled by a General Electric Volt-Pac variable transformer. An 8-point recorder allowed multiple temperature monitoring of the capsules with chromel-alumel thermocouples which were welded to the stainless steel capsules.

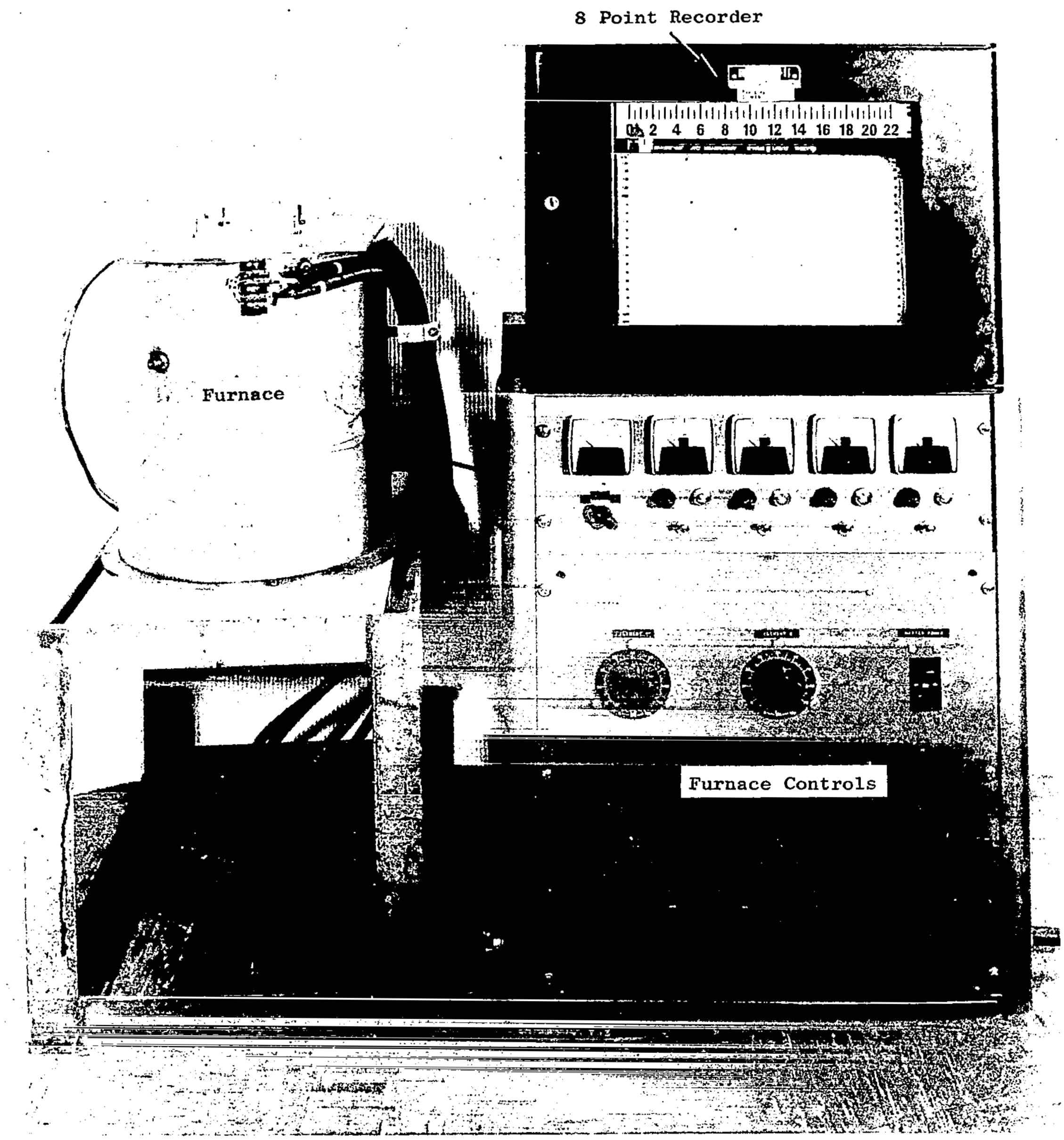


Figure 3. Test Facility for Isothermal Corrosion Capsule Tests. (C64121039)

VII. POSTTEST EVALUATION

After completion of the 1000-hour tests, the stainless steel capsules were removed from the furnace, opened, and the tantalum capsules removed. The tantalum capsules were then opened and the mercury drained from the capsules. A portion of the mercury drained from each capsule was reacted with nitric acid to form mercuric nitrate samples for spectrographic analysis. The samples were analyzed for Ta, Cb, W, Hf, and Zr, and the results are given in Table II. The erratic increase in tantalum concentration of the mercury is not completely understood, and although the capsules were opened with a tubing cutter, the contamination of the mercury by tantalum particles is a possible source.

The specimens were removed from the tantalum capsules, and the mercury film adhering to the bent specimens was removed by vacuum distillation in a Pyrex system using external infrared heaters and a mechanical vacuum pump. The temperature and pressure during the distillation were estimated at 200°F and 50 microns of mercury, respectively.

The cleaned specimens were then weighed, and no significant weight changes, i.e., $<$ ±0.02 percent, were observed.

Visual observation of the test specimens was performed at magnifications of 3x and 100x, and no cracks or changes in surface appearance were observed. Subsequently, all of the specimens were examined using a postemulsification fluorescent penetrant technique to detect any surface cracks. No cracks were found.

TABLE II.

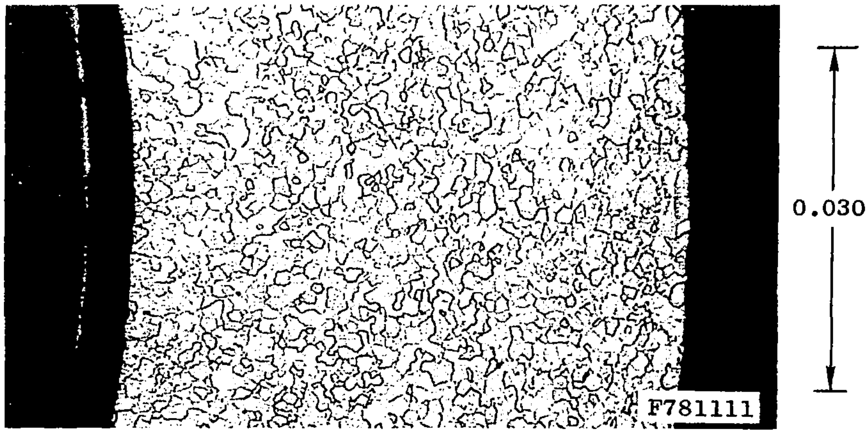
POSTTEST SPECTROGRAPHIC ANALYSIS OF MERCURY REMOVED FROM THE TANTALUM CAPSULES

	Concentration, ppm			
		For Capsules Containing		
Element	Pretest	Ta Specimens	T-111 Alloy Specimens	Cb-1Zr Specimens
Ta	ND[a]	140[b]	10[b]	100[b]
W	ND	< 6	< 6	< 6
Hf	-	< 6	< 6	< 6
Cb	ND	< 2	< 2	< 2
Zr	ND	< 2	< 2	< 2

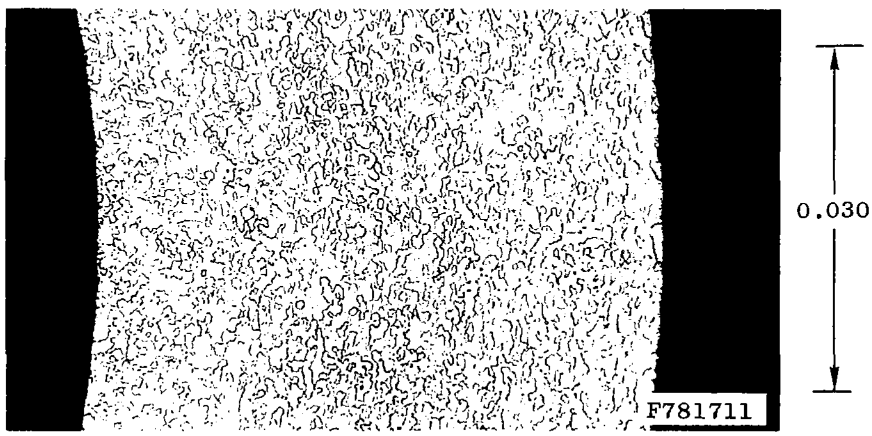
(a) ND - not detected

(b) The erratic increase in tantalum concentration is possibly a result of contamination of the mercury by tantalum during the opening of the capsules with a tubing cutter.

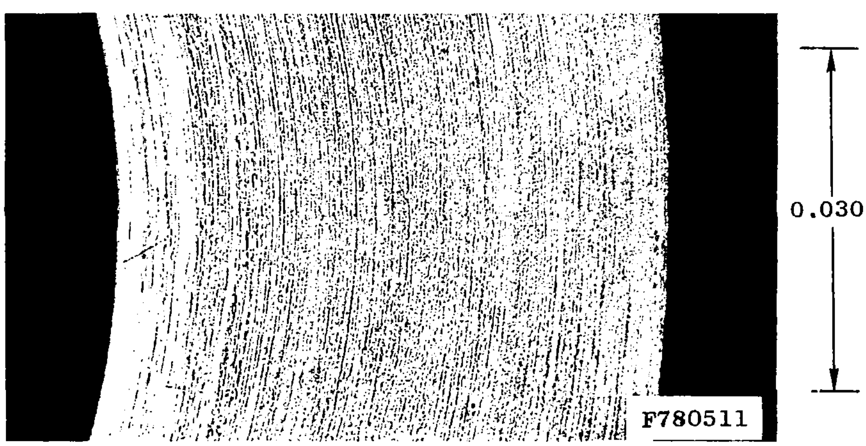
Metallographic examination of the specimens strained 20 percent by bending before exposure revealed no corrosion or other changes in microstructure as a result of the exposure to mercury at 1200°F for 1000 hours. Similar results were obtained for specimens strained 5 percent and all the specimens which had been annealed prior to testing. Typical photomicrographs of the most severely strained specimens after mercury exposure are shown in Figure 4. The Cb-1Zr specimen was actually strained greater than 20 percent before exposure since the as-received material was not in the recrystallized condition. Although the strain level is not known exactly, no corrosion was observed in any of the Cb-1Zr specimens. It should be noted that the failure to detect any cracking in the as-bent Cb-1Zr and T-111 alloy specimens exposed to mercury in this study is in direct contrast to the previously discussed results reported by Weeks.[1]



Unalloyed Ta Etchant: $30g NH_4F$ + $50ml HNO_3$ + $20ml H_2O$



T-111 Alloy Etchant: $50g NH_4F$ + $50ml HNO_3$ + $20ml H_2O$



Cb-1Zr Alloy Etchant: 60ml Glycerine + $20ml HNO_3$ + 20ml HF

Figure 4. Microstructure of Ta, T-111, and Cb-1Zr Alloy Specimens Strained 20% and Exposed to Liquid Mercury at 1200°F for 1000 Hours. (The Cb-1Zr Alloy is not Recrystallized) and Therefore the Actual Strain Present is > 20%.

APPENDIX A

Quality Assurance Data for 0.040-Inch-Thick T-111 Alloy Sheet

Material Control No. - 02C-002-2

Heat No. - 65080

Chemical Analyses

Ingot (Vendor Analysis)

Sample	Concentration, Percent by Weight: 1	2	3	4
W	9.00	9.00	8.90	8.65
Hf	2.15	1.90	1.80	1.80
	ppm			
Al	<10	<10	<10	<10
C	<40	<40	<40	<40
Cb	740	740	840	860
Co	< 5	< 5	< 5	< 5
Cr	<10	<10	<10	<10
Cu	<20	<20	<20	<20
Fe	25	30	25	50
H	3.0	-	-	3.4
Mo	20	20	20	20
N	29	18	18	31
Ni	<10	<10	<10	<10
O	100	-	-	100
Si	<40	<40	<40	<40
Ti	<20	<20	<20	<20
V	<20	<20	<20	<20

Final Product

	Concentration, ppm: C	O	N	H
Vendor	<40	50	15	1.8
G.E.	21/21	32/33	3/3	<1/<1

Mechanical Properties

Room Temperature Tensile Properties (Vendor)

U.T.S., ksi	0.2% YS, ksi	Elongation, %
93.5/94.0	83.4/84.7	29/28

Stress Rupture Properties (Vendor)

Stress, ksi	Temperature, °F	Life, hrs
19/19	2400/2400	>20.1/>20.1

Hardness (Vendor)

Ingot - 207-229 BHN range, 217 BHN average

Final Product - Surface - 235 DPH
Center - 237 DPH

Bend Properties (Vendor)

2 specimens - 1 T bend, 180°, no cracking

Metallography

% Recrystallization - Vendor - 100%
G.E. - 100%

Grain Size (ASTM) - Vendor - 9
G.E. - Trans. 7-8
Long. 7-8

Nondestructive Tests (Vendor)

Ultrasonic - No rejectable indications

Fluorescent Dye Penetrant - No rejectable indications

Final Anneal

1 hour at 3000°F at 1 x 10^{-4} torr

Quality Assurance Data for 0.040-Inch-Thick Tantalum Sheet

Material Control No. - 09A-036-1

Heat No. - 7565

Chemical Analyses - Final Product

	Concentration, ppm	
	Vendor	G.E.
O	62	68/67
N	30	47/47
H	-	1/1
C	24	23/25
Al	< 10	-
Cb	25	-
Cr	< 1	-
Cu	< 1	-
Fe	8	-
Mo	< 10	-
Ni	4	-
Si	12	-
Ti	< 5	-
W	< 40	-

Mechanical Properties

Room Temperature Tensile Properties (Vendor)

UTS, ksi	0.2% YS, ksi	Elongation,%
54.0	40.1	32

Metallography (G.E.)

100% Recrystallized

Grain Size (ASTM - Trans. - 7
Long. - 7

Quality Assurance Data for 0.040-Inch-Thick Cb-1Zr Alloy Sheet

Final Product Chemistry

	Concentration, ppm
C	37/34
O	188/183
N	45/52
H	5/2

Quality Assurance Data for 1.0-Inch-OD x 0.100-Inch-Thick Wall Tantalum Tubing

Material Control No. - 09A-038-(1-20)

Heat No. - 7566

Chemical Analyses

	Ingot Concentration, ppm	Final Product Concentration, ppm	
	Vendor	Vendor	G.E.
O	81	86	43/73
N	13	19	6/14
H	1.9	1.9	1/1
C	36	21	31/41
B	< 1	-	-
Al	< 10	< 10	-
Ca	< 25	< 25	-
Co	< 5	< 5	-
Cr	< 1	< 1	-
Cu	< 1	< 1	-
Fe	7	15	-
Hf	< 50	-	-
Cb	< 25	< 25	-
Mg	< 1	< 1	-
Mn	< 1	< 1	-
Mo	10	10	-
Ni	4	11	-
Pb	< 1	< 1	-
Si	16	15	-
Sn	< 1	< 1	-
Ti	< 5	< 5	-
V	< 5	-	-
W	< 40	< 40	-
Zr	< 50	-	-

Mechanical Properties

Room Temperature Tensile Properties (Vendor)

U.T.S., ksi	0.2% YS, ksi	Elongation, %
48.5/48.5	36.8/37.2	52/38

Hardness (Vendor)

Final Product - Vickers - 204

R_B - 48 - 50

Metallography (G.E.)

100% Recrystallized

Grain Size (ASTM) - Trans. - 7
Long. - 7

Nondestructive Tests (Vendor)

Fluorescent Dye Penetrant - No rejectable indications

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