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UNITED STATES ATOMIC ENERGY COMMISSION

THE CORROSION OF ZIRCONIUM IN 600°F
WATER AND IN 750°F SUPERHEATED STEAM

By
H. A. Pray
R. S. Peoples

January 15, 1951

Battelle Memorial Institute
Columbus, Ohio

Technical Information Service, Oak Ridge, Tennessee

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2

THE CORROSION OF ZIRCONIUM IN 600°F. WATER
AND IN 750°F. SUPERHEATED STEAM

Contract No. W-7405-eng-72

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January 15, 1951

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
INTRODUCTION.	5
EXPERIMENTAL WORK	14
Test Apparatus and Procedures.	14
Test Results	17
DISCUSSION.	29

SUMMARY

A comparison of the corrosion behavior of identical samples of zirconium was made between the 600°F. (1500 p.s.i.) water test and the 750°F. (1500 p.s.i.) steam test. The samples represented as-deposited iodide zirconium; arc-melted iodide zirconium; as-deposited and arc-melted iodide zirconium in which the nickel content varied from 8 to 750 p.p.m.; nitrogen-treated arc-melted iodide zirconium containing 0, 1, 3, and 5 per cent tin; and alloys prepared from induction-melted plate which was made by consumable electrode melting of Bureau of Mines sponge and represented tin levels of 0.0, 6.20, 8.94, 10.80, and 24.60 per cent.

Some conclusions may be drawn from the comparison. The appearance of white oxide or "breakdown" in resistance of zirconium (arc-melted, iodide, or alloyed zirconium) in 600°F. water at unpredictable times is accelerated by exposure to the 750°F. steam test. Zirconium which shows poor resistance after 18 hours' exposure to 750°F. steam will eventually show poor resistance (white oxide or breakdown) to 600°F. water. Exposure to 750°F. steam is undoubtedly a more severe test condition. Zirconium, which retained good resistance in 600°F. water for long-test periods, failed in 750°F. steam after 18 hours. It was also evident that zirconium which showed poor resistance to 600°F. water always showed poor resistance to 750°F. steam.

The test apparatus and procedures used in conducting both tests are described in detail.

INTRODUCTION

In the past several months, considerable effort has been devoted to the study of the corrosion behavior of as-deposited and arc-melted iodide zirconium in 600°F. distilled water. Based on a large number of tests, it has been shown that the resistance of zirconium in a short-time test (e.g., 350 hours or less) does not necessarily give an accurate indication of the corrosion behavior for more extended exposure periods.

In fact, it has frequently been observed that a zirconium sample which has shown excellent resistance for a period of, say, 1000 hours will suddenly "breakdown" and corrode at a high rate. In other words, to specify corrosion quality in the 600°F. water test, the length of test period, the rate for the test period, time to "breakdown", and rate after "breakdown" should be reported. Some examples of this type of behavior are shown in Figures 1 and 2 (the data are contained in Tables 1 and 2). Figure 1 is a graph showing the corrosion resistance of samples representing eleven different as-deposited iodide bars. One sample (18-D-7) had poor resistance from the start, one failed at 500 hours, three failed at 750 hours, and two failed at 1200 hours, while four retained good resistance for 1600 hours. Chemical and spectrographic data for three of the specimens (J-2, J-7, 18-D-7) are contained in Table 7. No real differences in the chemistry of these three that would account for the differences in corrosion behavior are evident.

Figure 2 contains a graph showing the corrosion behavior of some arc-melted, forged and rolled iodide-zirconium ingots. As in the case of the as-deposited iodide samples, "breakdowns" in resistance are noted at

FIGURE 1 CORROSION BEHAVIOR OF AS-DEPOSITED IODIDE ZIRCONIUM DURING EXPOSURE TO 600°F WATER (1500 psi.)

FIGURE 2. CORROSION BEHAVIOR OF ARC-MELTED IODIDE ZIRCONIUM DURING EXPOSURE TO 600 °F WATER (1500 psi)

TABLE 1. WEIGHT-GAIN DATA IN MG./SQ.CM. FOR SAMPLES
REPRESENTING A NUMBER OF DIFFERENT AS-DEPOSITED
IODIDE CRYSTAL BARS AFTER EXPOSURE TO 600°F.
WATER (1500 p.s.i.)

Sample No.	Exposure Time, Hours					
	40	305	500	750	1217	1630
J-1	0.00	0.06	0.06	0.06	1.01	0.97
-2	0.03	0.11	0.09	0.09	0.74	1.50
-4	0.03	0.10	0.08	0.08	0.10	0.20
-5	0.03	0.13	0.13	0.12	0.10	0.23
-6	0.03	0.09	0.09	0.09	0.12	0.94
-7	0.03	0.08	0.07	0.08	0.10	0.63
-8	0.03	0.09	0.09	0.12	1.24	2.16
-10	0.03	0.07	0.07	0.08	0.18	0.23
-11	0.03	0.10	0.08	0.08	0.17	0.22
-12	0.05	0.11	0.11	0.40	0.97	1.61
	<u>74</u>	<u>350</u>	<u>950</u>	<u>1240</u>	<u>1340</u>	
18-D-7	0.17	0.27	0.70	1.12	1.53	

TABLE 2. WEIGHT-GAIN DATA IN MG./SQ.CM. FOR SAMPLES OF
ARC-MELTED, ROLLED, AND FORGED ZIRCONIUM INGOTS
AFTER EXPOSURE TO 600°F. (1500 p.s.i.) WATER

Ingot No.	Exposure Time, Hours									
	50	150	192	250	400	513	666	1016	1236	3574
Z 510	0.12	-	0.16	-	0.16	-	0.16	0.16	0.15	0.45
Z 518	0.13	0.13	0.13	0.16	0.40	0.58	0.94	1.84	6.78	-
Z 521	0.13	0.13	0.13	0.13	0.21	0.24	0.51	1.18	1.60	-
Z 649	0.22	0.42	-	-	0.75	-	-	-	-	-
Z 627	0.15	0.24	-	-	0.29	-	0.29	1.00	-	-
Z 572	0.07	-	-	-	0.07	-	0.20	0.90	1.01	-
	<u>45</u>	<u>170</u>	<u>260</u>	<u>345</u>	<u>610</u>	<u>910</u>	<u>1410</u>	<u>1695</u>		
C-23	0.05	0.28	0.34	0.65	1.35	2.25	3.31	4.00		

unpredictable exposure times. Some failed after relatively short exposures (Z649, C-23), others after somewhat longer exposures, while Z510 still showed a good corrosion rate and no white oxide after 3574 hours.

It should not be construed that the above examples, illustrating the erratic and spotty corrosion behavior of zirconium in 600°F. water, are the few "unusual" cases observed. Numerous other examples have been noted. Table 3 contains a summary of the corrosion behavior in 600°F. water of 83 arc-melted iodide-zirconium samples and 451 as-deposited iodide-zirconium samples. The data are arranged according to test groups. A test group includes those samples exposed at the same time and in the same bomb. For each group, the number of samples tested is recorded, the duration of the test, the number and per cent which showed no white oxide or "breakdown" for the test duration, and the number and per cent which showed "breakdown" or white oxide at the indicated exposure period. Of the 83 arc-melted specimens, 40 or 48.1 per cent showed white oxide and breakdown in corrosion resistance at some unpredictable exposure time. Of these 40, 7 or 17.6 per cent failed within a 2-week test period, while 33 or 82.4 per cent failed some time after 2 weeks' exposure. In the case of the 451 as-deposited specimens, 198 (44.0 per cent) showed white oxide at some unpredictable time and of these 198, 142 (71.8 per cent) showed white oxide within a 2-week period, while 56 or 28.2 per cent failed after 2 weeks' exposure. Considering both arc-melted and as-deposited specimens (534 samples), 238 (44.5 per cent) showed white oxide or exhibited a "breakdown" in resistance and, of this number, 149 or 62.7 per cent would have been rejected in a 2-week test, while 89 or 37.3 per cent would have passed such a test. It can be noted from Table 3 that all the specimens

TABLE 3

Test Group No.	No. of Specimens in Group	Test Duration, Hrs.	Per Cent and No. of Spec. Showing No White Oxide for Test Duration		Per Cent and Number of Specimens in Test Group Showing "Breakdowns" or the Appearance of White Oxide During the Indicated Exposure Periods (Hours)											
					0 to 350 Hrs.		351 to 1000 Hrs.		1001 to 2000 Hrs.		2001 to 3000 Hrs.		3001 to 4000 Hrs.		4001 to 5000 Hrs.	
					No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
<u>Arc-Melted Iodide Zirconium</u>																
1	8	6624	0	0.0	0	0.0	3	37.5	2	25.0	2	25.0	0	0.0	1	12.5
2	9	6278	1	11.3	1	11.3	4	44.4	3	33.3	0	0.0	0	0.0	0	0.0
3	6	2117	0	0.0	1	16.7	2	33.3	3	50.0	0	0.0	0	0.0	0	0.0
4	8	3245	1	12.5	0	10.0	3	37.5	3	37.5	0	0.0	1	12.5	0	0.0
5	7	2276	7	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
6	10	2796	1	10.0	4	40.0	4	40.0	1	10.0	0	0.0	0	0.0	0	0.0
7	14	2635	14	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
8	21	3301	19	90.4	1	4.8	1	4.8	0	0.0	0	0.0	0	0.0	0	0.0
Summary	83		43	51.9	7	8.4	17	20.5	12	14.4	2	2.4	1	1.2	1	1.2
<u>As-Deposited Iodide Zirconium</u>																
1	2	5107	1	50.0	0	0.0	1	50.0	0	0.0	0	0.0	0	0.0	0	0.0
2	7	4785	7	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
3	3	3603	3	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
4	4	6085	2	50.0	2	50.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
5	1	3623	1	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
6	2	4265	1	50.0	1	50.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
7	3	4295	2	66.7	0	0.0	0	0.0	1	33.3	0	0.0	0	0.0	0	0.0
8	12	1630	5	41.7	0	0.0	5	41.7	2	16.6	0	0.0	0	0.0	0	0.0
9	1	4017	1	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
10	7	1787	7	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
11	144	1581	131	91.0	0	0.0	11	7.6	2	1.4	0	0.0	0	0.0	0	0.0
12	27	1884	2	7.2	0	0.0	23	85.1	2	7.2	0	0.0	0	0.0	0	0.0
13	8	3351	3	37.5	4	50.0	0	0.0	1	12.5	0	0.0	0	0.0	0	0.0
14	41	1332	37	90.2	0	0.0	4	9.8	0	0.0	0	0.0	0	0.0	0	0.0

TABLE 3. (Continued)

Test Group No.	No. of Specimens in Group	Test Duration, Hrs.	Pcr Cent and No. of Spec. Showing No White Oxide for Test Duration		Per Cent and Number of Specimens in Test Group Showing "Breakdowns" or the Appearance of White Oxide During the Indicated Exposure Periods (Hours)											
					0 to 350 Hrs.		351 to 1000 Hrs.		1001 to 2000 Hrs.		2001 to 3000 Hrs.		3001 to 4000 Hrs.		4001 to 5000 Hrs.	
					No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
15*	27	1177	0	0.0	27	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
16	28	1082	28	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
17*	101	731	0	0.0	100	99.0	1	1.0	0	0.0	0	0.0	0	0.0	0	0.0
18	13	995	11	84.0	2	16.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
19	2	2635	2	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
20	1	2495	1	100.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
21	5	2185	1	20.0	3	60.0	1	20.0	0	0.0	0	0.0	0	0.0	0	0.0
22	3	1451	1	33.3	2	66.7	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
23	3	1316	1	33.3	1	33.3	1	33.3	0	0.0	0	0.0	0	0.0	0	0.0
24	6	518	5	83.2	0	0.0	1	16.8	0	0.0	0	0.0	0	0.0	0	0.0
Summary	451		253	56.0	142	32.0	48	10.7	8	1.8	0	0.0	0	0.0	0	0.0

* Oxide-filled cracks.

in Groups 15 and 17 (as-deposited iodide) exhibited oxide-filled cracks within a two-week test period. Such cracks were present on the surface of the samples prior to testing. Eliminating these samples on the basis that they do not represent present iodide production, the analysis would become: of a total of 406 arc-melted and as-deposited iodide specimens, 110 (27.1 per cent) showed white oxide or exhibited a "breakdown" in resistance and, of this number, 21 (19.0 per cent) would have been rejected in a two-week test, while 89, or 81 per cent, would have passed such a test.

The conclusion should not be drawn that arc melting, forging, or rolling is responsible for the erratic behavior of the ingots. A rather rigorous experiment was recently conducted which demonstrated that arc melting and fabricating by the procedures used does not adversely affect the corrosion resistance of good-quality iodide zirconium.

It is thus evident that the corrosion of zirconium in 600°F. water for times longer than three weeks may be substantially greater than would be predicted at two weeks, and that even longer tests fail to predict for still longer times. If zirconium were selected for a reactor solely on the absence of visible white film after two weeks in 600°F. water, it is possible that a substantial white corrosion product will form on some of this material during the life of the reactor. It is obvious that a short-time test which will reliably reveal the long-time corrosion behavior is greatly to be desired.

Previous work showed that raising the test temperature to 650°F. (2200 p.s.i.) of either water or wet steam did not result in any marked acceleration of the corrosion of good-quality zirconium. Consequently, more drastic test conditions were sought. It was felt that this could

possibly be accomplished by exposure to temperatures above the critical point of water (706°F.). The conditions selected were 750°F. superheated steam at 1500 p.s.i., and the results of these studies are contained herein.

EXPERIMENTAL WORK

Test Apparatus and Procedures

The apparatus for conducting tests in 750°F. steam (1500 p.s.i.) is the same as that used for 600°F. water studies, namely, high-pressure autoclaves. A single unit consists essentially of a main autoclave body, a closure, a large nut to secure the closure to the body, the necessary gaskets and bolts for assembling, a pressure gauge,^a/thermocouple well, and a stand housing a heating well which, in turn, accommodates the autoclave body. The closure, body, and thermocouple well are constructed of Type 316 stainless steel, the gaskets of nickel, and the connections, safety assembly, and gauges of Type 304 stainless. The electric heating well for a standard one-liter autoclave has six strip heaters, each of 350-watt capacity attached, which is sufficient to provide the desired temperature. The temperature is maintained and controlled by a Foxboro potentiometer controller. Figure 3 shows a view of a bomb disassembled, together with the stand housing the heating well. The top of the stand is located at "A" and the heating well at "B" in the photograph, while an autoclave body is at "C", a large nut at "D", a closure with specimens mounted for testing at "E", and a nickel gasket at "F".

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FIGURE 3. VIEW OF AUTOCLAVE ASSEMBLY

556 110

In conducting tests in either 600°F. water or 750°F. superheated steam, the zirconium samples, either as-deposited iodide or arc melted, are machined to the desired shape and size, degreased in acetone, and then pickled to remove any possible damaged layer. Samples are pickled for three minutes in a solution containing 50 ml. of concentrated HNO_3 - 50 ml. of water - 6 grams of NH_4F per 100 cc. They are rinsed immediately in water. This operation removes approximately 2 mils from the surface. After pickling, the samples are dried, weighed, and mounted on the closure head utilizing Chromal A-type wire hooks and mica sheet to insulate the specimens from the bomb. Specimens mounted on the closure head may be seen located at "E" in Figure 3. The specimens shown in the photograph are approximately $1-1/4"$ x $1/2"$ x $0.020"$ and are typical of the size used in most of the tests about to be described.

After predetermined exposure periods to either 600°F. water (1500 p.s.i.) or 750°F. steam (1500 p.s.i.), the amount of corrosion taking place is determined by weight gain.

In conducting the 600°F. water tests, 600 ml. of water (distilled) is added to a one-liter body; then the closure is placed carefully on the body and held securely in place with the large nut. The pressure gauge and safety device are then mounted on the closure head and the entire assembly placed in the electric heating well. Operating at 600°F. with the above amount of water contained in the bomb, a gauge pressure of 1500 p.s.i. will then be indicated.

The 750°F. superheated steam test is conducted in essentially the same manner, with the following exceptions. The test is conducted by first adding 155 ml. of distilled water to a one-liter autoclave (proportioned

volumes to bombs of different capacity). When the autoclave temperature is between 250°F. and 300°F., steam is bled off, purging the bomb of air. The steam is condensed and measured, so that approximately 55 ml. are left in the system. This quantity of water results in a pressure of 1500 p.s.i. at 750°F.

In determining the corrosion behavior of any material in any medium, securing representative and identical samples is an extremely important problem. This is particularly true in the case of zirconium. A vast amount of data have been secured on as-deposited iodide zirconium, which shows that the corrosion quality not only varies along the length and cross section of individual bars but from bar to bar and from run to run. This variation in quality and the related sampling problem make it extremely difficult to obtain a direct and valid comparison between the two test conditions under consideration. As nearly identical specimens as possible were used in the following comparative experiments.

Test Results

The results of the studies in 750°F. superheated steam have indicated that zirconium can be evaluated rapidly for service in 600°F. water. The test will readily distinguish between areas of good and poor corrosion quality on iodide-crystal bar, arc-melted or extruded material.

Table 4 contains corrosion data for 34 as-deposited iodide-zirconium and 4 arc-melted samples after exposure to 600°F. water and to 750°F. steam. These samples represent some 25 iodide-crystal bars and 4 arc-melted ingots. The behavior of the samples was established first in 600°F. water (1500 p.s.i.). They were then cleaned mechanically to remove

18

TABLE 4. CORROSION DATA BASED ON WEIGHT GAIN FOR AS-DEPOSITED AND ARC-MELTED IODIDE-ZIRCONIUM SAMPLES AFTER EXPOSURE TO 600°F. WATER (1500 p.s.i.) AND 750°F. STEAM (1500 p.s.i.)

500°F. later (1500 p.s.i.)										750°F. Steam	
Sample No.	Ni Content, p.p.m.	Rate at 350 Hours, Mg/Sq Cm/Mo	"Breakdown" or Appearance of White Oxide	Rate Before "Breakdown", Mg/Sq Cm/Mo	Rate Immediately After "Breakdown", Mg/Sq Cm/Mo	Duration of Test, Hours	Rate for Entire Test Period, Mg/Sq. Cm/Mo	Final Appearance of Specimen	Wt. Gain in Mg/Sq Cm/Mo, 10 Hours' Exposure	Final Appearance of Specimen	
As-deposited Iodide Zirconium											
N-2	5	0.10	-	-	-	1787	0.21	Dark film	0.08	Dark film	
N-5	5	0.09	-	-	-	1787	0.22	Ditto	0.13	Dark film	
4-4	10	0.26	-	-	-	1540	0.15	"	0.25	Mottled white oxide	
40A-4	20	0.11	-	-	-	4700	0.07	"	0.12	Dark film	
4-1	36	0.27	-	-	-	1540	0.11	"	0.35	Ditto	
40-5	30	0.17	-	-	-	1540	0.08	"	0.10	"	
40-4	40	0.15	-	-	-	1540	0.08	"	0.22	"	
40-1	90	0.26	-	-	-	1540	0.07	"	0.24	Mottled white oxide	
40-8	50	0.17	-	-	-	1540	0.09	"	0.34	Mottled white oxide	
40-1	80	0.14	-	-	-	1540	0.06	"	0.21	Dark film	
5-1	110	0.88	50	-	-	1190	-	White oxide	0.24	White oxide	
V-1	200	0.22	-	-	-	1540	0.08	Dark film	2.00	White oxide	
1-4	290	0.12	-	-	-	1540	0.11	Ditto	0.27	Mottled white oxide	
LM-3 (910-1-2)	290	0.11	-	-	-	4874	0.05	"	0.17	Dark film	
V-8	450	0.20	-	-	-	1540	0.09	"	0.27	Mottled white oxide	
V-4	500	0.19	-	-	-	1540	0.08	"	1.34	White oxide	
3	560	0.15	-	-	-	1540	0.07	"	1.40	Ditto	
0-3	750	0.22	350	0.22	0.80	1574	-	White oxide	1.27	"	
Arc-melted Iodide Zirconium											
Z-732	100	0.10	-	-	-	1235	0.12	Dark film	0.42	Streak- white oxide	
CZ-30 (Arc-melted)	146	1.05	50	0.58	1.21	310	-	White oxide	2.04	White oxide	
CZ-23 (Arc-melted)	300	0.45	745	0.45	1.70	310	-	Mottled white oxide	1.78	Mottled white oxide	
CZ-26 (Arc-melted)	300	0.25	910*	-	-	310	2.22	Light white oxide	1.50	Mottled white oxide	
As-deposited Iodide Zirconium											
J-4	30	0.24	-	-	-	1030	0.09	Dark film	0.20	Dark film	
J-10	400	0.17	-	-	-	1030	0.10	Ditto	0.10	Ditto	
J-11	110	0.24	-	-	-	1540	0.16	"	0.15	"	
J-5	110	0.21	-	-	-	1030	0.10	"	0.37	White oxide	
J-1	40	0.14	730	0.05	1.45	1540	-	White oxide	0.89	Ditto	
J-2	55	0.20	730	0.10	1.01	1540	-	Ditto	1.77	"	
J-5	40	0.21	1217	0.09	1.42	1030	-	"	0.14	"	
J-7	20	0.13	1217	0.03	0.93	1030	-	"	1.52	"	
J-3	30	0.21	730	0.11	1.74	1030	-	"	1.32	"	
J-12	15	0.20	300	0.14	1.40	1030	-	"	1.75	"	
18-A-7	20	0.21	350	0.21	0.38	1340	-	White oxide	0.95	White oxide	
18-D-7	10	0.56	350	-	-	1340	-	Ditto	1.02	Ditto	
18-T-1	20	0.40	350	0.40	0.74	1340	-	"	0.93	"	
4-5	700	0.16	-	-	-	1340	0.15	Dark film	0.14	Dark film	
5-5	90	0.25	-	-	-	1340	0.17	Ditto	0.23	Ditto	
5-3	450	0.21	-	-	-	1340	0.21	"	0.15	"	

* This specimen showed a very light white oxide at 910 with little weight gain

any corrosion film or product, re-pickled, and exposed to 750°F. superheated steam.

In the case of the specimens identified with the letter J, four (J-4, -10, -11, and -5) had excellent resistance to 600°F. water after 1630 hours' exposure, while the remaining six specimens showed "breakdowns" (and white corrosion product) between 750 and 1630 hours' exposure. After 18 hours' exposure to 750°F. steam, three of the four which showed good resistance to 600°F. water were in excellent condition (no white corrosion product), and those which had failed after extended exposure to 600°F. water showed white corrosion product and high weight gain. In the case of Specimen J-5 (the one which showed good resistance to 600°F. water after 1630 hours' exposure and failed after 18 hours at 750°F.), failure or breakdown in resistance might have been expected eventually in 600°F. water.

The seven specimens (including J-5) which performed poorly in both tests were cleaned and re-exposed to steam. They were examined at predetermined periods up to 18 hours. It was revealed (data included in Table 5) that these materials were defective at periods shorter than 18 hours.

The data for the specimens identified as 18-A, -D, -T, -4, etc., (Table 4) again show that the same relationship exists between the two tests. Of the six specimens, the three showing good resistance to 600°F. water after 1340 hours' exposure were in excellent condition after 18 hours in 750°F. steam, while the three exhibiting "breakdowns" in 600°F. water (between 350 and 950 hours' exposure) showed poor resistance (white corrosion product) to 750°F. steam after 18 hours. The appearance of these

TABLE 5. WEIGHT-GAIN DATA FOR AS-DEPOSITED IODIDE-ZIRCONIUM SAMPLES AFTER EXPOSURE TO 750°F. STEAM (1500 p.s.i.) FOR PERIODS UP TO 18 HOURS

Sample No.	Exposure Time, Hours								
	1	2	3	4	5	7	10	14	18
J-1	0.16	0.29	0.41	0.54	0.66	0.95	1.23	1.64	1.93
-2	0.25	0.44	0.56	0.69	0.78	1.13	1.47	1.91	2.19
-5	0.27	0.42	0.57	0.77	0.88	1.11	1.42	1.76	2.19
-6	0.17	0.30	0.43	0.56	0.60	0.90	1.16	1.50	1.80
-7	0.41	0.45	0.57	0.73	0.85	1.18	1.38	1.83	2.11
-8	0.25	0.36	0.41	0.51	0.66	0.97	1.22	1.68	2.04
-12	0.20	0.33	0.45	0.57	0.69	1.02	1.35	1.79	2.29

specimens after 72 hours in 750°F. steam may be seen in Figure 5.

Many of the specimens listed in Table 4 showed excellent resistance to 600°F. water for periods of two months or longer but turned white after only 18 hours' exposure to steam. This would indicate, as in the case of Specimen J-5, that, if these specimens had been exposed for a longer period of time to 600°F. water, they would have eventually shown a breakdown and white product. It is important to note that none of the specimens which exhibited poor resistance to 600°F. water were resistant to 750°F. steam.

A recent investigation* seemed to indicate an inhibiting effect of nickel on the corrosion rate of zirconium in 750°F. steam. In view of this, the nickel content for each specimen is included in Table 4, and it can be seen that a range of 8 to 750 p.p.m. nickel is represented. Of the 38 specimens listed in the table, 18 have a nickel content less than 90 p.p.m., while 20 have a content of 90 p.p.m. or greater. In the case of those with a nickel content less than 90 p.p.m., 6 showed a dark film (good resistance) after 18 hours' exposure to 750°F. steam, while 12 showed white oxide (poor resistance). Of those with a nickel content of 90 p.p.m., or greater, 12 exhibited white product and 8 the dark film associated with good corrosion resistance. These results show no relationship between nickel content and corrosion behavior in 750°F. steam. Specimens 8-1, 0-3, CZ-30, CZ-29, and CZ-28 with nickel contents in p.p.m. of 110, 750, 140, 300, and 500, respectively, which showed poor resistance to 600°F. water, also showed poor resistance and white oxide in 750°F. steam. Considering all specimens, none can be noted which had poor resistance to

* MIT-DSK-1.

72759

FIGURE 4. PHOTOGRAPH SHOWING APPEARANCE OF ARC-MELTED IODIDE-ZIRCONIUM SPECIMENS AFTER 72 HOURS' EXPOSURE TO 750°F. SUPERHEATED STEAM (1500 p.s.i.)

72759

FIGURE 5. PHOTOGRAPH SHOWING APPEARANCE OF AS-DEPOSITED IODIDE-ZIRCONIUM SAMPLES AFTER EXPOSURE TO 750°F. SUPERHEATED STEAM (1500 p.s.i.). SPECIMENS 4-5, 5-5, AND 6-5 ARE SHOWN AT THE LEFT, WHILE 18-A-7, 18-D-7, AND 18-T-1 ARE SHOWN AT THE RIGHT.

water and good resistance to steam, regardless of the nickel content. A conclusion which may be drawn from these data is that the nickel content in this range has little or no affect on the corrosion rate in either test. There is no evidence in these results that nickel exerts an inhibiting effect on the corrosion of zirconium in 750°F. steam. This is not only true for the as-deposited material but for the arc-melted material (Specimens CZ-28, -29, and -30) to which nickel was intentionally added during melting.

In addition to the above data for as-deposited iodide zirconium, a considerable quantity of supporting evidence has been secured on arc-melted material. Samples of arc-melted, forged, and rolled sheet, representing some 40 ingots whose behavior had been established in 600°F. water, were exposed to 750°F. superheated steam. These samples represented both material which had excellent resistance to 600°F. water and material which showed "breakdowns" in resistance and localized corroded areas (white corrosion product) at unpredictable exposure times up to 3500 hours. Exposure to 750°F. steam for 18 hours disclosed the localized corroded areas. Figure 4 contains a photograph showing the appearance of some of these samples after 72 hours' exposure to superheated steam. The white corroded areas seen on the specimens match those, rather closely, outlined on the same specimens after extended exposure to 600°F. water. Figure 6 contains a photograph of a 2" x 4" arc-melted forged and rolled sheet specimen after exposure to 750°F. steam for 18 hours. Localized corroded areas are clearly outlined. This same specimen had withstood approximately 1200 hours' exposure to 600°F. water with no evidence of white corrosion product.

In another experiment, four samples of arc-melted and forged iodide-

73531

FIGURE 6. PHOTOGRAPH SHOWING APPEARANCE OF ARC-MELTED IODIDE ZIRCONIUM AFTER 18 HOURS' EXPOSURE TO 750°F. STEAM (1500 p.s.i.). THIS SAMPLE HAD PREVIOUSLY BEEN EXPOSED APPROXIMATELY 1200 HOURS TO 600°F. WATER WITH NO EVIDENCE OF WHITE CORROSION PRODUCT.

zirconium ingots* containing 0, 1, 3, and 5 per cent Sn were impregnated with nitrogen. All samples were treated in nitrogen in the same manner and at the same time to give an intended concentration of 1500 p.p.m. After nitrogen treatment, each sample was cut in half, one-half being exposed to 600°F. water and the other half to 750°F. steam. The appearance of the specimens after approximately 15 hours' exposure to the two test conditions is shown in Figure 7.

The cross section of the cylindrical samples is represented by the faces appearing in the photograph, and the depth of contamination by nitrogen can be seen. The appearance of the specimens in both tests is identical. The weight-gain data for these studies are contained in Table 6. It should be pointed out that, while it required essentially 1000 hours in 600°F. water to show a breakdown for the 3 per cent Sn alloy (Specimen Z-777), it required only 33 hours' exposure in 750°F. steam. It was known prior to this experiment that, for unalloyed zirconium, this nitrogen concentration would cause rapid failure in less than 24 hours' exposure to 600°F. water. The chemical and spectrographic data for these alloys are given in Table 7. It can be seen that, with the exception of tin content and tungsten in the case of the 5 per cent Sn alloy, no significant difference in the chemistry of the alloys exists.

Another series of alloys, representing tin levels of 0.00, 6.20, 8.94, 10.80, and 24.60 per cent, was corrosion tested in both 600°F. water and 750°F. steam. These alloys were prepared from induction-melted plate which was made by consumable-electrode melting of Bureau of Mines sponge, and which is known to have poor resistance to 600°F. water. The weight-

* Ingots were arc melted twice in a water-cooled copper crucible utilizing a tungsten electrode and a helium atmosphere.

				73035
% Sn	<0.05	1.01	2.98	4.91

FIGURE 7. PHOTOGRAPH SHOWING THE CROSS SECTION OF ARC-MELTED AND FORGED ZIRCONIUM-TIN ALLOYS TREATED IN NITROGEN AFTER EXPOSURE TO 750°F. STEAM (1500 p.s.i.) AND 600°F. WATER (1500 p.s.i.).

TABLE 6. WEIGHT GAIN DATA IN Mg/Sq.Cm FOR Zr-Sn ALLOYS EXPOSED TO
600°F. WATER (1500 p.s.i.) AND 750°F. STEAM (1500 p.s.i.)

Induction-Melted Hoover Plate																
600°F. Water (1500 p.s.i.)											750°F. Steam (1500 p.s.i.)					
Exposure Time, Hours											Exposure Time, Hours					
Sample No.	% Sn	43	80	145	200	300	500	810	1260	1620	54	72	90			
HP-0	<0.05	1.64	3.80	9.30	17.80	29.40	-	-	-	-	0.57	1.37	1.47			
-5	5.20	0.01	0.02	0.04	0.05	0.05	0.07	0.10	0.17	0.18	0.49	0.41	0.47			
-10	8.94	0.02	0.06	0.07	0.11	0.11	0.16	0.22	0.29	0.33	0.46	0.47	0.59			
-15	10.80	0.03	0.07	0.10	0.10	0.11	0.23	0.35	0.55	0.72	0.61	0.82	1.06			
-25	24.60	3.93	9.67	22.00	34.70	65.0	-	-	-	-	-	-	-			

Arc-Melted and Forged Iodide-Zirconium Nitrogen Treated to Give Concentration of 1500 p.p.m.																
600°F. Water (1500 p.s.i.)										750°F. Steam (1500 p.s.i.)						
Exposure Time, Hours										Exposure Time, Hours						
Sample No.	% Sn	20	60	173	253	364	564	1056	1456	15	33	51	39	87	135	153
CZ-761	<0.05	After 20 hrs. white ring								After 15 hrs. white ring						
-779	1.01	After 20 hrs. white ring								After 15 hrs. white ring						
-777	2.98	0.00	0.00	0.08	0.15	0.23	0.34	0.52	0.70	0.06	0.88	1.21	1.14(Flaking)			
-780	4.91	0.00	0.00	0.05	0.15	0.20	0.25	0.37	0.47	0.00	0.07	0.12	0.22	0.22	0.57	0.63

TABLE 7. ANALYTICAL AND SPECTROGRAPHIC DATA

Sample No.	Element in p.p.m.																								
	C	N	Sn	Al	Fe	Ti	Si	Mn	Cu	Pb	Cr	Cd	B	Mg	Ca	Mo	Ni	V	Be	W	HF	Ta	Co	Zn	
										As-deposited Iodide															
J-2	300	10	<10	100	100	<10	100	<1	5	5	10	<10	3	20	<10	65	35	<10	<1	<50	24,500	-	-	-	
J-7	200	10	<10	50	70	25	110	<1	7	5	10	<10	4	10	<10	75	20	<10	<1	<50	23,000	-	-	-	
18-A-7	190	6	<5	30	450	<10	90	<5	10	40	90	<10	100-1000	<10	<10	20	700	<10	<1	<50	24,000	<500	<5	<100	
18-D-7	230	5	<5	40	360	<10	110	<5	10	30	20	<10	2	<10	<10	10	90	<10	<1	<50	21,000	<500	<5	<100	
18-T-1	190	5	<20	60	270	<10	100	<5	5	20	100	<10	3	<10	<10	10	450	<10	<1	<50	21,000	<500	<5	<100	
4-5	190	12	<5	50	270	<10	130	<5	10	20	<10	<10	5	<10	<10	20	20	<10	<1	<50	26,000	<500	<5	<100	
5-5	240	22	5	50	200	<10	90	<5	10	10	<10	<10	2	<10	<10	<10	10	<10	<1	<50	27,000	<500	<5	<100	
6-5	400	11	5	60	270	<10	90	<5	5	10	<10	<10	1	<10	<10	<10	20	<10	<1	<50	21,000	<500	<5	<100	
										Induction-melted Hoover Plate															
HP-0	3300	200	10	250	1000	50	70	5	5	30	50	<10	2	50	<10	10	10	<10	<1	<50	8,000	<500	<5	-	
HP-5	3700	370	62,000	300	1300	40	80	5	10	40	40	<10	2	20	<10	10	<5	<10	<1	<50	8,000	<500	<5	-	
HP-10	3400	260	89,400	350	1300	40	100	5	10	40	50	<10	2	10	<10	10	<5	<10	<1	<50	8,000	<500	<5	-	
HP-15	3500	270	108,000	300	1400	40	70	5	10	50	50	<10	2	10	<10	10	<5	<10	<1	<50	8,000	<500	<5	-	
HP-25	3000	290	246,000	350	1400	40	100	5	20	50	50	<10	2	10	<10	10	<5	<10	<1	<50	7,900	<500	<5	-	
										Arc-melted and Forged Iodide-Zirconium Nitrogen Treated to Give Concentration of 1500 p.p.m.															
Z-781	500	70*	<500	40	340	<10	90	<5	10	<10	<10	<10	<1	10	<10	<10	20	<10	<1	120	700	<760	<5	-	
Z-779	250	70*	10,190	40	380	<10	100	<5	10	<10	<10	<10	<1	10	<10	<10	30	<10	<1	150	800	<500	<5	-	
Z-777	360	60*	29,800	40	400	<10	90	<5	10	<10	10	<10	<1	10	<10	<10	30	<10	<1	100	650	<500	<5	-	
Z-780	210	40*	49,100	40	320	<10	100	<5	<10	10	20	<10	<1	10	<10	20	30	<10	<1	1200	500	<500	<5	-	
										Arc-melted, Forged, and Rolled Iodide															
Z-510	260	60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<500	-	-	-	-	
Z-513	120	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<500	-	-	-	-	
Z-521	90	50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<500	-	-	-	-	

* Nitrogen content before treatment

gain data, after exposure to the two test conditions, are included in Table 6. The two tests evaluate the alloys in like manner. In both tests, the 0.0 and the 24.6 per cent Sn alloys are the least resistant, followed by the 10.8, 8.94, and 6.20 per cent Sn in that order. Table 7 contains the analytical data for these materials. It is interesting to note that the 6.20 per cent Sn alloy has excellent resistance to both media, in spite of the high carbon and nitrogen contents.

As-deposited iodide-zirconium bars in their entirety and split in half longitudinally have been exposed to 750°F. steam. Twelve split bars which were reportedly of good corrosion quality, based on two weeks' exposure to 600°F. water, were mechanically cleaned, pickled, and exposed to steam. After 18 hours' exposure, over 50 per cent of the bars showed white corrosion product at various locations on both the split and crystal faces, indicating poor quality and nonuniformity in the material. Another 12 bars (6 pounds in weight), which had not been previously tested in 600°F. water, were exposed to steam. After 18 hours' exposure, approximately 65 per cent (by weight) of the zirconium showed white corrosion product and would have been rejected by this test method.

DISCUSSION

On the basis of the experiments described, the 750°F. steam test discloses the corrosion characteristics of zirconium (crystal bar, arc melted, extruded, or fabricated) in a very considerably shorter time than the 600°F. water test. Raising the test temperature from 600°F. to 750°F. without changing the pressure accelerates attack (with no apparent change

in mechanism) on zirconium which exhibits poor resistance to 600°F. water, or that which shows "breakdowns" after extended exposure.

Zirconium which shows good corrosion resistance (no corrosion product and very little weight gain) after 18 hours' exposure to 750°F. steam will, in all probability, withstand long exposures to 600°F. water. On the other hand, zirconium which shows poor resistance and white oxide after 18 hours in steam at 750°F. will, at some unpredictable time, show poor resistance to 600°F. water. The steam test will reject zirconium which would withstand considerable exposure to 600°F. water. However, it has not, in our present experience, accepted material rejected by the 600°F. water test.

As a result of experience here with the test, we believe that it is a useful laboratory tool.

The use of the accelerated test as a routine acceptance test for as-deposited crystal bar from current production is under investigation at WAPD*. Preliminary results indicate a considerably higher per cent of rejections than for the presently used two-week 600°F. water test. This is in line with the results described in this report.

The period covered for this report is from October, 1949, to December, 1950. Data are recorded in Laboratory Record Books Nos. 4802, pp. 24 to 100; 5133, pp. 1 to 100; 5414, pp. 1 to 100; and 5632, pp. 1 to 50.

* WAPD-MM-68.