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Argonne National Laboratory

THE CORROSION OF THORIUM

A Review of Project Literature

by

J. E. Draley

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H. F. Canell

Chief, Declassification Branch *Ret*

THE CORROSION OF THORIUM

A Review of Project Literature

by

J. E. Draley

METALLURGY DIVISION

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THE CORROSION OF THORIUM

A Review of Project Literature

by

J. E. Draley

Abstract

A project literature search disclosed considerable inconsistency in the aqueous corrosion of thorium, depending on metal source and sample preparation.

Corrosion rates of representative metal in distilled water were of the order of 4 to 10×10^{-3} mg/cm²/hr at 100°C, and 0.7 mg/cm²/hr at 178°C.

Attempts to increase the corrosion resistance of thorium were generally unsuccessful; instead corrosion rates usually were increased. Exceptions seemed to include the addition of a small amount of either beryllium or carbon.

Abstracts are given of project literature concerning reaction of thorium and an alloy with gases.

Introduction

For some time thorium metal has been considered for use in nuclear reactors. The nuclear reactions taking place within the metal would make its use very similar to that of uranium in reactors, and the requirements for prevention of fission product recoil and of corrosion would be about the same. Consequently, there has been and is interest in its corrosion behavior. The usefulness of water as a coolant has resulted in a demand for information concerning the resistance of thorium and its alloys to aqueous corrosion.

This report has as its object the summarizing of all project literature dealing with the aqueous corrosion of thorium and its alloys. Considerably less information was available than for uranium and its alloys. Significant results have been reported from the Metallurgical Laboratory, University of Chicago; Oak Ridge National Laboratory; and Iowa State College.

The problem of determining the rate of reaction of thorium or alloys was more difficult because its metallurgy had not been as well worked out. In general there were two kinds of metal available for study: cast thorium made at Iowa State College (Ames) and hot-pressed powder metallurgy metal made at Westinghouse. Purity in the former was not uniform, depending on when the metal had been prepared; porosity and poor bonding were evident in the latter. Thorium characteristically corrodes in water to form relatively insoluble ThO_2 . This corrosion product sometimes forms an adherent protective film which prevents rapid corrosion of the metal. When the sintered metal is corroded, protection is observed to be rather poor, and the corrosion product consisted of a mixture of metal and ThO_2 for the only case where identification was reported (CT-3036). Apparently corrosion proceeded around metal particles and loosened them before they were completely oxidized.

Although no detailed description or discussion of results of tests on air scaling and reaction with hydrogen will be given, brief abstracts of project references on these subjects are in the appendix of this report, pages 22-23.

Test Methods

In preparation for test, clean surfaces were producible only by mechanical means (BMI-76). For most tests, only one exposure time was reported. Samples were removed after this exposure, dried, and weighed. In some instances, attempts were made to remove the adhering products of corrosion. At the Metallurgical Laboratory, chemical and electrochemical stripping methods included immersion in fluoride-containing nitric acid solutions and anodizing in sodium hydroxide solution. In both procedures, it was necessary to determine when the oxide was gone and attack of the clean metal started. At Ames several mechanical methods were used in efforts to remove the corrosion product.

In either case, weighing the unattacked metal after test allowed determination of the amount of metal corroded. When results after only one time were available, the average rate of metal loss from the beginning of the test could be computed. This is not designated "corrosion rate" in this report, since it is not useful in specifying an actual rate of reaction at any known time and cannot be used to obtain the amount of corrosion to be expected at any other time, except in the rather unusual case when the reaction rate is the same at all times.

Some data are available for which tests of different duration were run. When each sample was stripped of corrosion product and the actual weight of metal corroded was determined, slopes of the linear portions of the curves are referred to as "corrosion rates."

Results

Corrosion of Thorium in Distilled Water: Changes in corrosion behavior are shown in Table I for samples of the same material in distilled water at 95°C. No surface treatment was used on the samples: they were put into test as received and weighed after exposure, with drying the only treatment. Rather large weight losses made unnecessary the removal of the amount of corrosion product adhering after test for the degree of accuracy desired. The water was not changed during test. The considerable changes in the amount of corrosion as a function of mechanical treatment were ascribed to the degree of cold working of the metal. It is not impossible that the effect was due simply to the amount of operational handling, perhaps the working of oxide into the metal. In any case the sensitivity to metal handling or preparation is evident.

Corrosion rates of metal available to those testing can be estimated in boiling distilled water from the data in Figure 1. Samples were ground before test and chemically or electrochemically cleaned after test, before weighing (CT-3036). Water quality was maintained by continuous replenishment. Some of the points used for the curve for Westinghouse sintered metal are for the metal as received, and some were obtained after hot rolling. For this material, hot rolling is observed to have caused relatively little change in corrosion behavior. Both for Westinghouse sintered metal and for Ames metal, a period of rapid initial reaction was followed by a lower rate. The estimated rate for the Westinghouse sintered metal is about two and one-half times that for Ames metal. When some Westinghouse metal was remelted, its corrosion in boiling distilled water roughly approximated that of the Ames metal tested.

The results of testing the same materials in distilled water in Pyrex beakers in a steam autoclave at 178°C are shown in Table II. Samples were periodically removed, dried, weighed, and placed back in test. Again the Ames metal and remelted Westinghouse metal were considerably better than Westinghouse sintered metal. For the better samples, Figure 2 shows that reaction was apparently quite slow for several days and then increased in rate, suddenly for the Ames metal, and more gradually for remelted Westinghouse metal. After fifteen or twenty days the rates of weight loss appear to be the same, about 0.7 mg/cm²/hr.

At 315°C, observed attack was extremely rapid (BMI-76, p. 30).

Thorium in Solutions: Test results of exposure to simulated Columbia River water are given in Table III. Samples were ground clean before test and then weighed after the 16 days test before and after chemically removing the corrosion product. Solution flow rate past the samples, in the all-glass test loops, was 20-25 ft/second. Referring to Figure 1, the average rates of metal loss from the start of test until 16 days in nearly stagnant boiling

Table I

CORROSION OF THORIUM IN DISTILLED WATER AT 95°C

Test Duration: 30 Days

Reference: ORNL-1066

Metal	Average rate of wt. change, mg/cm ² /hr, x 10 ³
Ames W (1)	- 0.443 - 0.369
Ames C (2)	- 8.19 - 8.46
Ames W (3)	-25.7 -16.5
Ames W (4)	- 7.19 - 5.97
Ames W (5)	- 0.221 - 0.329
No. 3 (6)	- 0.155 - 0.099
A592 (7)	-10.00 - 8.00

- (1) Ames W: Early Ames production, rolled at Westinghouse, annealed, cold rolled 68%, and annealed one hour at 750°C in vacuo.
- (2) Ames C: Late shipment of Ames cast metal. These samples cold rolled 75% and annealed at 750°C for 30 minutes in vacuo.
- (3) Cold rolled 86% and annealed at 750°C for 30 minutes in vacuo.
- (4) Cold rolled 86%.
- (5) Cold rolled 25%.
- (6) Ames W remelted and cast in ZrO₂ under argon, cold rolled 68%, annealed 1 hour in vacuo at 750°C.
- (7) Ames metal remelted and cast in ZrO₂ in vacuo, hot rolled 80%, cold rolled 40%, and annealed 1 hr in vacuo at 750°C.

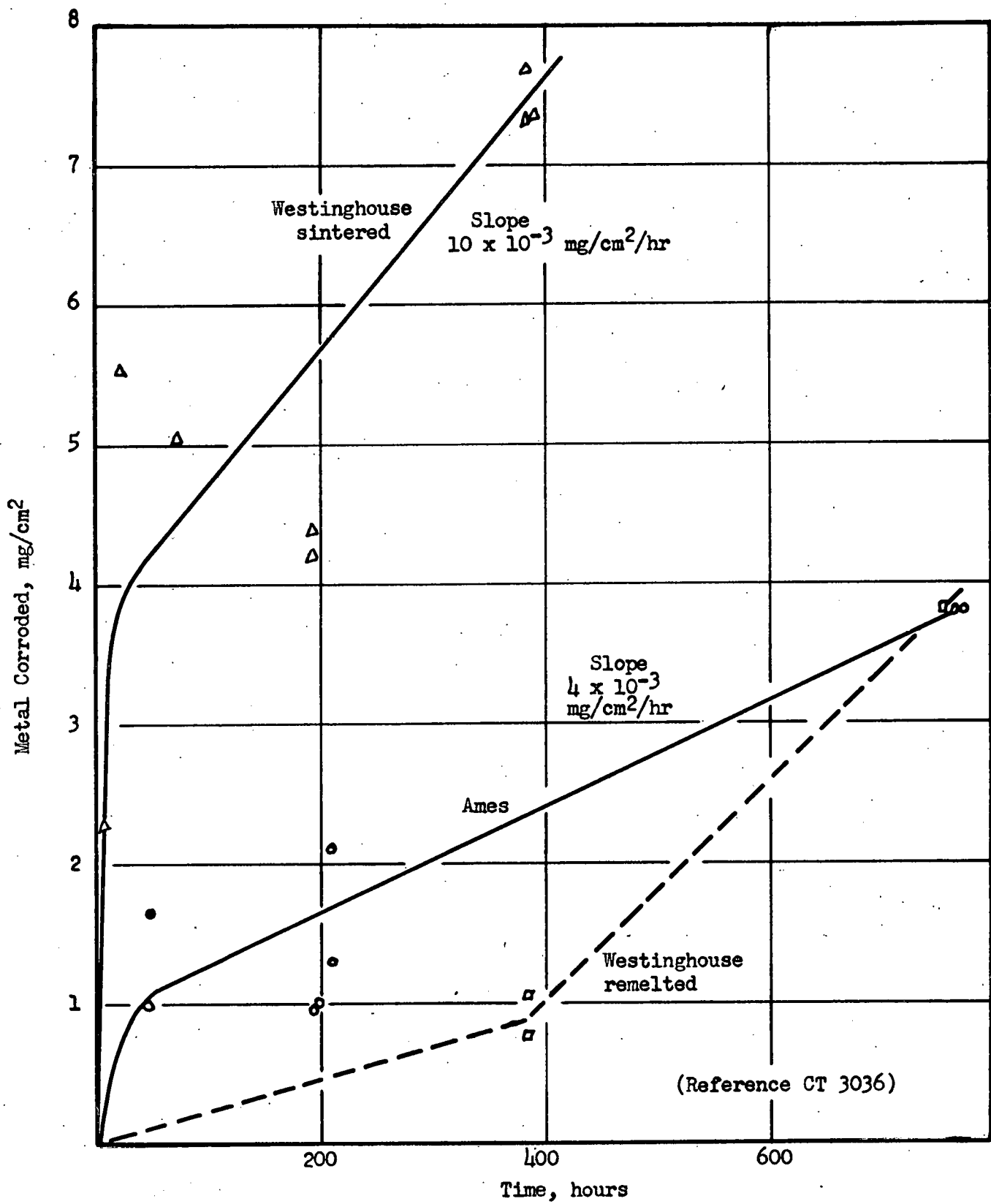


Figure 1

CORROSION OF THORIUM IN BOILING DISTILLED WATER

Table II

AUTOCLAVE TESTING OF THORIUM IN WATER (178°C)

Reference: CT-3036

Metal \ Test Duration	Weight change, mg/cm ² , uncleaned specimens					
	1 day	2 days	4 days	8 days	16 days	32 days
Extruded Ames metal	+0.29	+0.77	+0.14	-105	-270	-551
Westinghouse sintered	-565	-1360	Completely corroded in 3 days			
Westinghouse sintered and hot rolled	-980	Completely corroded in 2 days				
Remelted Westinghouse sinter	+0.47	0.00	-0.40	-12.3	-94.3	-348

distilled water were 20×10^{-3} and 6.3×10^{-3} mg/cm²/hr, for Westinghouse and Ames metal. In both aerated and hydrogenated solution, the combined effects of lowering the temperature to 70°, adding several solutes, and operating at relatively high flow rates were undetectable.

Considerably higher rates were observed when nearly the same solution (higher pH) was used in an essentially stagnant test at 70°C, as shown in Table IV. The corrosion observed was about twenty-five times that from the high flow rate systems for Ames metal and about 7.5 times that for Westinghouse metal. Rates were roughly the same for the two kinds of metal in the stagnant test.

Coupling with Aluminum: It was reported (CT-2715) that connecting pieces of aluminum and thorium in water at 100° and at 140°C increased the aluminum corrosion somewhat but had no significant effect on corrosion of the thorium. Evidently the aluminum was anodic to the thorium in the tests run.

Thorium Alloys in Distilled Water: The corrosion resistance of a number of alloys in distilled water was investigated at 95°C. No sample surface preparation was used before or after test. Results are listed in Table V. Because of uncertainty in the rate for unalloyed metal, as previously discussed in connection with Table I, very little can be said as to the effects of the alloying constituents. Harmful additions perhaps include 6% Cb, 2% Ti, 1% Ti plus 2% Zr.

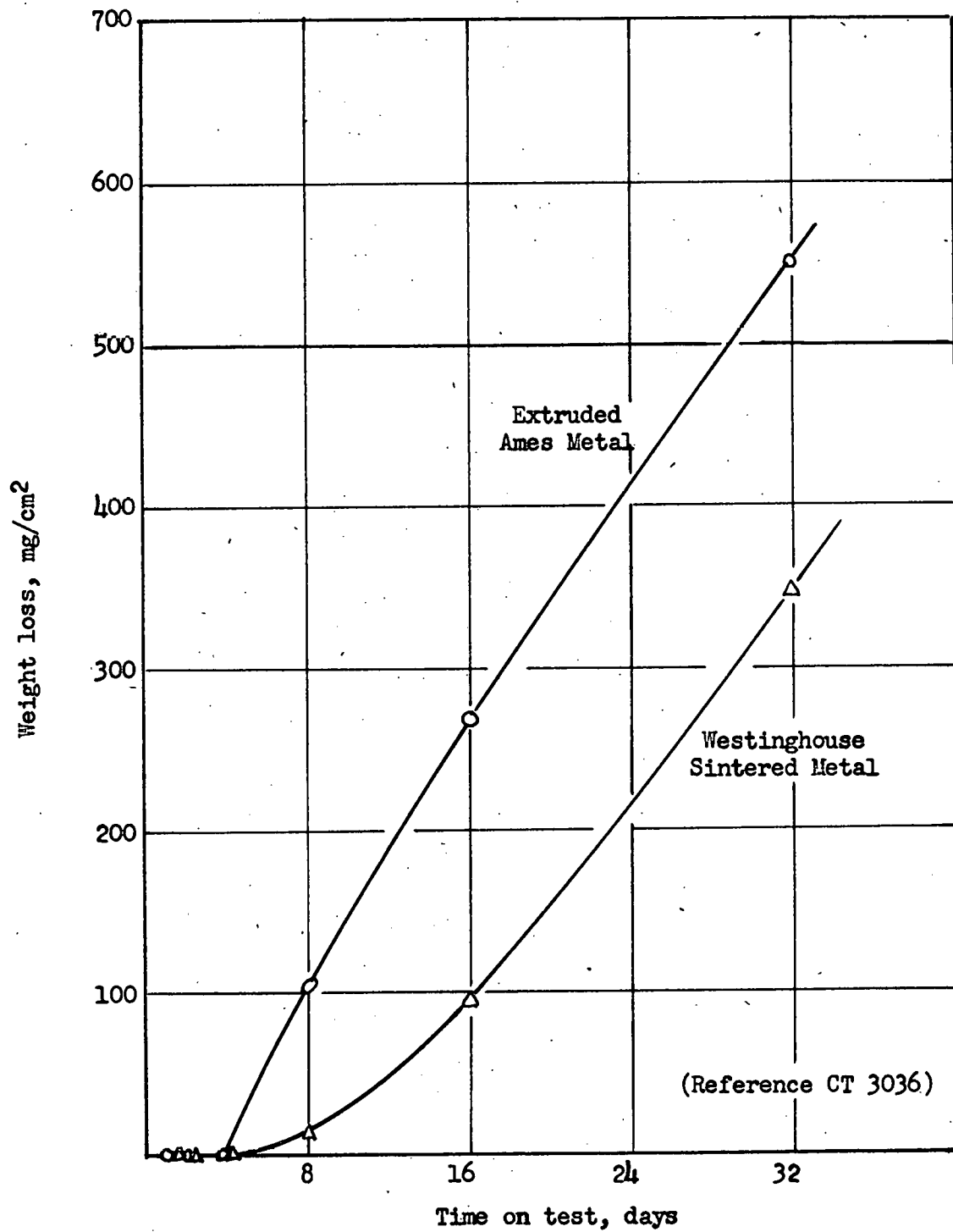


Figure 2

CORROSION OF THORIUM IN DISTILLED WATER
AT 178°C

Table III

**CORROSION OF THORIUM AND THORIUM ALLOY
IN FLOW SYSTEM**

Simulated Columbia River Water Plus 1 ppm Cl^- and 6×10^{-3} N H_2O_2
at pH 6.5, 70°C, 20-25 ft/sec. -- 16 Day Test

(CT-3036)

Metal	Average rate of weight loss from start of test, $\text{mg}/\text{cm}^2/\text{hr}$		
	uncleaned	clean	
<u>Aerated Solution</u>			
A-1 Ames Cast 2 spec.	5.6×10^{-3} 0.3×10^{-3}	10.0×10^{-3} 4.9×10^{-3}	7.5×10^{-3} Avg.
W-1 Westinghouse 2 spec.	2.9×10^{-3} 4.1×10^{-3}	27.0×10^{-3} 18.0×10^{-3}	22.5×10^{-3} Avg.
<u>Hydrogenated Solution</u>			
A-1 Ames cast 2 spec.	0.6×10^{-3} 2.2×10^{-3}	4.9×10^{-3} 8.1×10^{-3}	6.5×10^{-3} Avg.
W-1 Westinghouse 2 spec.	6.2×10^{-3} 12.0×10^{-3}	15.0×10^{-3} 31.0×10^{-3}	23.0×10^{-3} Avg.
<u>Aerated Solution</u>			
Westinghouse sintered + 0.6 wt. % U (3 specimens)			17.5×10^{-3} Avg.

Table IV

STATIC CORROSION OF THORIUM

Simulated river water plus 1 ppm Cl^- and 1.2×10^{-3} NH_2O_2 , aerated,
pH 7.5, 70°C

Reference: CT-3036

Material	Wt. losses, mg/cm^2	Time, hrs	Average loss from start of test, $\text{mg}/\text{cm}^2/\text{hr}$	
			clean	uncleaned
Ames	13.8	397	170×10^{-3}	80×10^{-3}
Ames	43.7	397	180×10^{-3}	110×10^{-3}
Westinghouse	28.6	397	140×10^{-3}	72×10^{-3}
Westinghouse	62.3	397	200×10^{-3}	157×10^{-3}

Table V

CORROSION OF THORIUM ALLOYS IN DISTILLED WATER AT 95°C

Test Duration: 30 days

Reference: ORNL-1066

Alloy	Treatment	Average rate of weight change, mg/cm ² /hr, x 10 ³
2% Cr*	1	- 0.096
		- 0.143
4% Cr	1	- 0.290
		- 0.081
2% Cb	1	+ 0.557
		+ 0.101
4% Cb	1	+ 1.393
		+ 0.822
4% Cb	2	- 6.17
		- 3.83
6% Cb	2	-11.35
		-18.62
2% Zr	1	- 3.18
4% Zr	1	- 0.710
		- 0.044
4% Zr	2	- 3.29
		- 3.68
6% Zr	2	- 4.90
		- 5.99
2% Ti	1	+40.6
4% Ti	2	- 7.47
		- 8.68
6% Ti	2	+19.7
		- 0.81
1% Ti, 1% Zr	2	- 3.90
		- 3.49

*By weight

Table V (Cont'd)

Alloy	Treatment	Average rate of weight change, mg/cm ² /hr, x 10 ³
1% Ti, 2% Zr	2	Disintegrated Disintegrated
2% Ti, 1% Zr	2	-10.90 -10.39
4% ti, 1% Zr	2	- 0.60 - 6.79

Treatments

(1) Ames metal remelted and cast in ZrO₂ under vacuum cold rolled 68%, and annealed at 750°C for 1 hour in vacuum.

(2) Ames metal remelted and cast in ZrO₂ under vacuum, cold rolled 75%, and annealed at 750°C for 30 minutes in vacuum.

Of the alloys tested in water at 178°C at another laboratory (Table VI), those which seemed to offer considerably improved corrosion resistance contained small amounts of beryllium or carbon. Of particular interest may be the apparent difference in corrosion between a 1.6% Be alloy melted in graphite and the same alloy melted in beryllia.

Using different mechanical methods of removing the corrosion product, the data in Tables VII and VIII were obtained. Rates of corrosion cannot be estimated with any accuracy, but in several cases alloy corrosion was considerably more severe than that of the parent metal. In no case is it certain that alloying with beryllium improved the corrosion resistance.

The corrosion of beryllium alloys in steam at 100° and 140°C is reported in Table IX. Samples were not cleaned after test: weight changes were divided by the exposure time to give the rates in the last column. The amount of corrosion cannot be deduced well from the data available, but minimum attack seems to have occurred with a relatively small amount of beryllium in the alloy.

Table VI

CORROSION OF THORIUM ALLOYS IN WATER (178°C)

(Autoclave Tests)

Reference: CT-3036

Time in test Alloy	Weight change, mg/cm ² , based on uncleaned specimens						Clean (1) Specimens
	0.8 days	1.7 days	4 days	8 days	16 days	32 days	32 days
Blank (Westinghouse Thorium) (2)	0.47	0.00	- 0.04	- 12.3	- 94.3	-348.	
1.08 w/o Si	0.51	0.69	1.0	- 39.2	-171.	-495.	
2 w/o Si	0.20	0.26	1.0	- 9.3	-106.	-339.	
4.3 w/o Si	0.0	- 0.28	0.03	- 12.3	- 74.	-249.	
0.62 w/o Si + 1.11 w/o Be	- 0.58	- 1.0	- 0.96	- 0.83	- 3.8	+ 0.4	-15.0
0.4 w/o Be	0.46	1.7	1.65	5.0	7.0	+ 28.	- 7.7
0.94 w/o Be	0.32	- 0.13	(3)c.c.	----	----	----	
1.6 w/o Be; melted in graphite	- 0.02	- 0.63	- 0.72	- 1.0	- 0.9	- 0.6	- 9.0
1.6 w/o Be, melted in BeO	- 0.36	- 0.23	3.4	c.c.	----	----	
2.46 w/o Be	- 0.55	- 1.2	- 1.1	- 0.97	- 0.6	- 0.7	-46.
2.02 w/o Cb	- 4.6	- 18.	- 59.3	-153.5	-328.	-673.	
4.17 w/o Cb	-73.	-179.	-503.	c.c.	----	----	
2.75 w/o Fe	0.25	- 45.6	-114.	-242.	-573.	c.c.	
5.53 w/o Fe	0.50	1.1	- 0.87	- 1.7	-255.	c.c.	
0.3 w/o C	- 0.09	- 0.4	- 0.16	- 0.69	- 0.4	- 0.7	-11.0
1.24 w/o C	0.0	c.c.					
0.6 w/o U	----	19.0	c.c.				

(1) Cleaned with 70% HNO₃ plus 0.1% NaF at 115°C.

(2) Ingot analyzed 300 ppm Be at top and 20 ppm Be at bottom. Corrosion specimen taken from middle of ingot.

(3) c.c. means specimen was completely corroded.

Table VII

CORROSION OF THORIUM AND THORIUM-BERYLLIUM ALLOYS
IN WATER AT 100°C

Reference: CT-2715

Composition, % Be	Length of test, hrs	Average rate of weight gain, mg/cm ² /hr, × 10 ³			
		Method 1	Method 2	Method 3	Method 4
0	90	+1.03	- 1.71	-3.09	-22.3
0.5	90	+ .85	- 1.13	-1.97	-44.0
1.0	91	-	+11.10	+1.72	-88.0
2.0	91	No change	zero	zero	-56.8

Methods:

- 1: Sample removed, washed, dried, and weighed.
- 2: Sample, when dried, brushed off with camel's hair brush and weighed.
- 3: Sample polished on wheel fitted with non-metal-cutting wool cloth (AB Miracloth) and weighed.
- 4: Sample polished to bright metallic luster on wheel fitted with 000 emery polishing paper and weighed.

Table VIII

CORROSION OF THORIUM AND THORIUM-BERYLLIUM ALLOYS
IN WATER

Reference: CT-2715

Composition, % Be	Length of test, hrs	Average rate of weight gain, mg/cm ² /hr, x 10 ³			
		Method 1	Method 2	Method 3	Method 4
		<u>at 140°C</u>			
0	138	+ 1.64	- 0.99	- 2.52	- 48.9
0.5	138	-747.	-787.	-817.	-1110.
1.0	138	+ 5.45	+ 3.89	+ 1.17	- 106.
2.0	138	+ 10.73	+ 9.1	+ 7.68	- 66.
		<u>at 180°C</u>			
0	71	+ 2.34	- 7.04	- 8.98	- 68.7
2.0	70	-	-	- 95.2	- 415.

Methods:

- 1: Sample removed, washed, dried, and weighed.
- 2: Sample, when dried, brushed off with camel's hair brush and weighed.
- 3: Sample polished on wheel fitted with non-metal-cutting wood cloth (AB Miracloth) and weighed.
- 4: Sample polished to bright metallic luster on wheel fitted with 000 emery polishing paper and weighed.

Table IX

CORROSION OF THORIUM-BERYLLIUM ALLOYS IN STEAM

Reference: CS-2614

Wt % Be	Time, hours	Wt. change, mg/cm ² /hr, x 10 ³
<u>At 100°C, 1 atmosphere pressure</u>		
0.0	193	+ 1.365
0.519	214	- 0.583
1.033	214	- 0.066
1.80	216	+ 0.081
3.04	225	+ 0.282
3.59	214	+ 0.322
<u>At 149°C, ca. 30 psig</u>		
0	64	+ 0.508
0.519	64	+ 0.197
1.033	64	+ 0.329
1.80	64	+ 0.404
3.04	64	+ 0.364
3.59	64	+ 0.260

Beryllium Alloy in Various Solutions: An alloy containing 0.5 w/o Be was tested in nitrates and nitric acid, as shown in Table X. The alloy, made with Ames metal, lost weight at a rate of 5 to 7 times that in water for the more dilute solutions, dissolving much more rapidly in concentrated nitric acid.

Discussion

Information available is insufficient to draw conclusions as to the essential features which influence the corrosion behavior of thorium. A definite increase in aqueous corrosion rate is shown when the temperature is increased from 100° to 178°C.

It is possible that the wide variation in corrosion behavior observed for different metal samples has been due chiefly to the oxygen and/or carbon content of the metal. The Ames metal used was characteristically much higher in carbon and lower in oxygen than the Westinghouse metal. Analytical difficulties have been considerable, and the content of these elements has not been known accurately.

Further evidence concerning the point is the reduction in metal corrosion caused by the addition of small amounts of beryllium and carbon, elements with a high affinity for oxygen. Evidence is too scanty to conclude whether the effect of carbon is simply to reduce the oxygen content of the metal, although the loss of corrosion resistance caused by further carbon addition suggests that the presence of carbon is not particularly desirable. Careful preparation of metal specimens of known composition would allow clarification of this point.

The dependence of corrosion on cold work reported in Table I might have been due to the amount of oxygen worked into the surface metal, or the oxidation that took place during the annealing operations. The fact that no surface metal was removed before the single exposure to distilled water leads to the belief that no conclusions should be drawn about comparative results of the test. Surface oxidation before test does influence the corrosion observed; for example, anodic pretreatment has been reported as reducing the attack by water (CT-3054). Such behavior is perhaps only temporary, and long tests, with periodic weighing, might give much more reproducible results. Even under most favorable testing procedures, only one exposure time can give misleading results. If an eight-day test had been run for the samples whose behavior was given by the top curve in Figure 1, "rates" determined would have been larger than the slope of the linear portion of the curve by a factor of seven or so; if the test had been for 24 days, such a "rate" would have been double the slope of the curve.

Table X

CORROSION OF Th/0.5 w/o Be ALLOY IN VARIOUS SOLUTIONS

Reference: CT-2715

Solution	Temp, °C	Time of test, hrs	Average rate of weight loss mg/cm ² /hr
0.3 M Uranyl) nitrate)	100	114	0.0655
0.1 M HNO ₃)			
0.3 M Thorium nitrate	100	114	0.0414
0.5 M Nitric acid	98	113	0.0483
Concentrated) (15.4 M)) Nitric acid)	86	113	1.235

The "induction period" of only slight corrosion during the initial part of the exposure is characteristic of fairly good quality metal. The cause of the phenomenon is not known, although it was presumed to have been caused by a protective surface layer, probably oxide produced by contact with air before test. The same behavior was exhibited when supposedly clean samples were exposed to purified hydrogen at 400°C (CT-3045).

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APPENDIX: ABSTRACTS FOR REACTION WITH GASES

Air

CT-2400: Ames cast thorium gained weight linearly with time after various induction periods at temperatures from 300 to 500°C. Rates are given very roughly by the equation:

$$\log G = 9.25 - \frac{6250}{T} \quad (G \text{ in mg/cm}^2/\text{hr}; T, \text{ degrees Kelvin})$$

A 2 w/o beryllium alloy showed essentially the same behavior from 400 through 450°C, following the equation

$$\log G = 5.55 - \frac{3910}{T} \quad (G \text{ in mg/cm}^2/\text{hr}; T, \text{ degrees Kelvin})$$

At 500°C, however, its rate of weight gain decreased after about 2 hours. The slope of the curve (straight line) subsequent to that time was too low to fit the log G equation above.

ME-110: Penetration rates for the oxidation of thorium in still air were 0.5, 15, 18 mm/year at 100, 200, 300°C, respectively.

CT-2893: Air scaling rates given for 300-900°C, and the effect of air velocity. For Ames and Westinghouse metal. Weight gains after 1/2 hour in several gases at 800°C were as follows:

Air	6.0 g/cm ² gain
Tank N ₂	4.4
Purified N ₂	2.0
Tank A	1.0
Purified A	0.75

Hydrogen

CT-3054: Equilibrium vapor pressure of hydrogen over thorium hydride, analyzed as $\text{ThH}_{3.2}$ is given by the equation:

$$\log P = 7.50 - \frac{2800}{T} \quad (P \text{ in mm Hg; } T, \text{ degrees K):}$$

CT-3045: After induction periods for freshly ground surfaces, depending on temperature, the linear absorption of hydrogen proceeded at the following rates, assuming the reaction product to be ThH_4 :

Temperature °C	Rate, mg Th/cm ² /hr		
	Westinghouse Metal	Ames Metal	Hot-wire Metal
505	129		174
475	109		
440	88.4		
425	84.5		
400	80	168	
180	19.7	23.6	
100	14.6		

The product took several days to be converted to ThO_2 by water at 178°C (See also CT-3036).

CS-2672: Reaction $\text{Th} + \text{H}_2$ is strongly exothermic, X-ray diagrams indicate formation of at least two hydride phases. Both phases and finely divided metal are pyrophoric.

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UNITED STATES ATOMIC ENERGY COMMISSION

THE CORROSION OF THORIUM
A Review of Project Literature

By
J. E. Draley

October 3, 1952

Argonne National Laboratory
Lemont, Illinois

Technical Information Service, Oak Ridge, Tennessee



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

THE CORROSION OF THORIUM

A Review of Project Literature

by

J. E. Draley

METALLURGY DIVISION

October 3, 1952

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4

THE CORROSION OF THORIUM

A Review of Project Literature

by

J. E. Draley

Abstract

A project literature search disclosed considerable inconsistency in the aqueous corrosion of thorium, depending on metal source and sample preparation.

Corrosion rates of representative metal in distilled water were of the order of 4 to 10×10^{-3} mg/cm²/hr at 100°C, and 0.7 mg/cm²/hr at 178°C.

Attempts to increase the corrosion resistance of thorium were generally unsuccessful: instead corrosion rates usually were increased. Exceptions seemed to include the addition of a small amount of either beryllium or carbon.

Abstracts are given of project literature concerning reaction of thorium and an alloy with gases.

Introduction

For some time thorium metal has been considered for use in nuclear reactors. The nuclear reactions taking place within the metal would make its use very similar to that of uranium in reactors, and the requirements for prevention of fission product recoil and of corrosion would be about the same. Consequently, there has been and is interest in its corrosion behavior. The usefulness of water as a coolant has resulted in a demand for information concerning the resistance of thorium and its alloys to aqueous corrosion.

This report has as its object the summarizing of all project literature dealing with the aqueous corrosion of thorium and its alloys. Considerably less information was available than for uranium and its alloys. Significant results have been reported from the Metallurgical Laboratory, University of Chicago; Oak Ridge National Laboratory; and Iowa State College.

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The problem of determining the rate of reaction of thorium or alloys was more difficult because its metallurgy had not been as well worked out. In general there were two kinds of metal available for study: cast thorium made at Iowa State College (Ames) and hot-pressed powder metallurgy metal made at Westinghouse. Purity in the former was not uniform, depending on when the metal had been prepared; porosity and poor bonding were evident in the latter. Thorium characteristically corrodes in water to form relatively insoluble ThO_2 . This corrosion product sometimes forms an adherent protective film which prevents rapid corrosion of the metal. When the sintered metal is corroded, protection is observed to be rather poor, and the corrosion product consisted of a mixture of metal and ThO_2 for the only case where identification was reported (CT-3036). Apparently corrosion proceeded around metal particles and loosened them before they were completely oxidized.

Although no detailed description or discussion of results of tests on air scaling and reaction with hydrogen will be given, brief abstracts of project references on these subjects are in the appendix of this report, pages 22-23.

Test Methods

In preparation for test, clean surfaces were producible only by mechanical means (BMI-76). For most tests, only one exposure time was reported. Samples were removed after this exposure, dried, and weighed. In some instances, attempts were made to remove the adhering products of corrosion. At the Metallurgical Laboratory, chemical and electrochemical stripping methods included immersion in fluoride-containing nitric acid solutions and anodizing in sodium hydroxide solution. In both procedures, it was necessary to determine when the oxide was gone and attack of the clean metal started. At Ames several mechanical methods were used in efforts to remove the corrosion product.

In either case, weighing the unattacked metal after test allowed determination of the amount of metal corroded. When results after only one time were available, the average rate of metal loss from the beginning of the test could be computed. This is not designated "corrosion rate" in this report, since it is not useful in specifying an actual rate of reaction at any known time and cannot be used to obtain the amount of corrosion to be expected at any other time, except in the rather unusual case when the reaction rate is the same at all times.

Some data are available for which tests of different duration were run. When each sample was stripped of corrosion product and the actual weight of metal corroded was determined, slopes of the linear portions of the curves are referred to as "corrosion rates."

Results

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Corrosion of Thorium in Distilled Water: Changes in corrosion behavior are shown in Table I for samples of the same material in distilled water at 95°C. No surface treatment was used on the samples: they were put into test as received and weighed after exposure, with drying the only treatment. Rather large weight losses made unnecessary the removal of the amount of corrosion product adhering after test for the degree of accuracy desired. The water was not changed during test. The considerable changes in the amount of corrosion as a function of mechanical treatment were ascribed to the degree of cold working of the metal. It is not impossible that the effect was due simply to the amount of operational handling, perhaps the working of oxide into the metal. In any case the sensitivity to metal handling or preparation is evident.

Corrosion rates of metal available to those testing can be estimated in boiling distilled water from the data in Figure 1. Samples were ground before test and chemically or electrochemically cleaned after test, before weighing (CT-3036). Water quality was maintained by continuous replenishment. Some of the points used for the curve for Westinghouse sintered metal are for the metal as received, and some were obtained after hot rolling. For this material, hot rolling is observed to have caused relatively little change in corrosion behavior. Both for Westinghouse sintered metal and for Ames metal, a period of rapid initial reaction was followed by a lower rate. The estimated rate for the Westinghouse sintered metal is about two and one-half times that for Ames metal. When some Westinghouse metal was remelted, its corrosion in boiling distilled water roughly approximated that of the Ames metal tested.

The results of testing the same materials in distilled water in Pyrex beakers in a steam autoclave at 178°C are shown in Table II. Samples were periodically removed, dried, weighed, and placed back in test. Again the Ames metal and remelted Westinghouse metal were considerably better than Westinghouse sintered metal. For the better samples, Figure 2 shows that reaction was apparently quite slow for several days and then increased in rate, suddenly for the Ames metal, and more gradually for remelted Westinghouse metal. After fifteen or twenty days the rates of weight loss appear to be the same, about 0.7 mg/cm²/hr.

At 315°C, observed attack was extremely rapid (BMI-76, p. 30).

Thorium in Solutions: Test results of exposure to simulated Columbia River water are given in Table III. Samples were ground clean before test and then weighed after the 16 days test before and after chemically removing the corrosion product. Solution flow rate past the samples, in the all-glass test loops, was 20-25 ft/second. Referring to Figure 1, the average rates of metal loss from the start of test until 16 days in nearly stagnant boiling

Table I

CORROSION OF THORIUM IN DISTILLED WATER AT 95°C

Test Duration: 30 Days

Reference: ORNL-1066

Metal	Average rate of wt. change, mg/cm ² /hr, x 10 ³
Ames W (1)	- 0.443 - 0.369
Ames C (2)	- 8.19 - 8.46
Ames W (3)	-25.7 -16.5
Ames W (4)	- 7.19 - 5.97
Ames W (5)	- 0.221 - 0.329
No. 3 (6)	- 0.155 - 0.099
A592 (7)	-10.00 - 8.00

- (1) Ames W: Early Ames production, rolled at Westinghouse, annealed, cold rolled 68%, and annealed one hour at 750°C in vacuo.
- (2) Ames C: Late shipment of Ames cast metal. These samples cold rolled 75% and annealed at 750°C for 30 minutes in vacuo.
- (3) Cold rolled 86% and annealed at 750°C for 30 minutes in vacuo.
- (4) Cold rolled 86%.
- (5) Cold rolled 25%.
- (6) Ames W remelted and cast in ZrO₂ under argon, cold rolled 68%, annealed 1 hour in vacuo at 750°C.
- (7) Ames metal remelted and cast in ZrO₂ in vacuo, hot rolled 80%, cold rolled 40%, and annealed 1 hr in vacuo at 750°C.

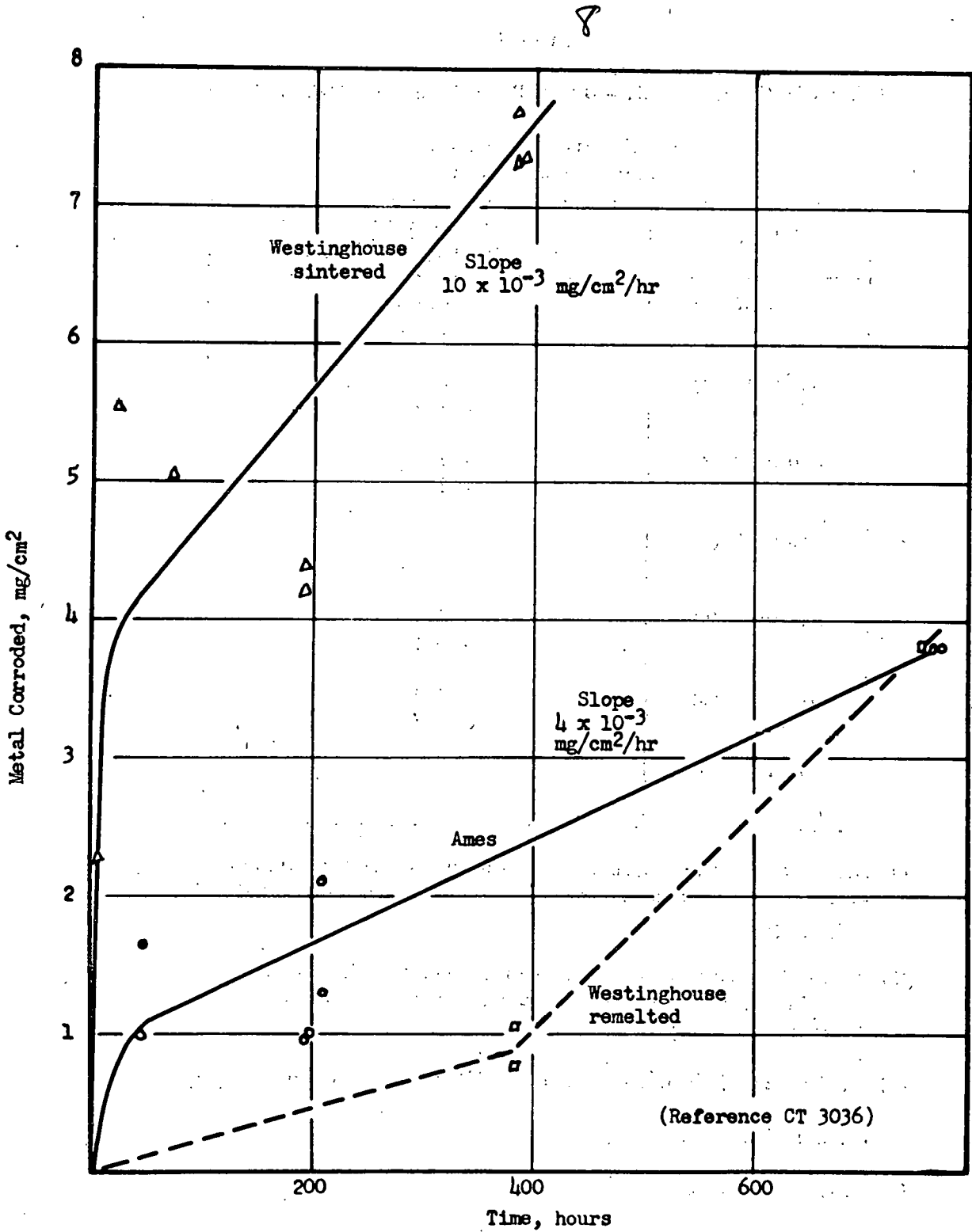


Figure 1

CORROSION OF THORIUM IN BOILING DISTILLED WATER

Table II

AUTOCLAVE TESTING OF THORIUM IN WATER (178°C)

Reference: CT-3036

Metal \ Test Duration	Weight change, mg/cm ² , uncleaned specimens					
	1 day	2 days	4 days	8 days	16 days	32 days
Extruded Ames metal	+0.29	+0.77	+0.14	-105	-270	-551
Westinghouse sintered	-565	-1360	Completely corroded in 3 days			
Westinghouse sintered and hot rolled	-980	Completely corroded in 2 days				
Remelted Westinghouse sinter	+0.47	0.00	-0.40	-12.3	-94.3	-348

distilled water were 20×10^{-3} and 6.3×10^{-3} mg/cm²/hr, for Westinghouse and Ames metal. In both aerated and hydrogenated solution, the combined effects of lowering the temperature to 70°, adding several solutes, and operating at relatively high flow rates were undetectable.

Considerably higher rates were observed when nearly the same solution (higher pH) was used in an essentially stagnant test at 70°C, as shown in Table IV. The corrosion observed was about twenty-five times that from the high flow rate systems for Ames metal and about 7.5 times that for Westinghouse metal. Rates were roughly the same for the two kinds of metal in the stagnant test.

Coupling with Aluminum: It was reported (CT-2715) that connecting pieces of aluminum and thorium in water at 100° and at 140°C increased the aluminum corrosion somewhat but had no significant effect on corrosion of the thorium. Evidently the aluminum was anodic to the thorium in the tests run.

Thorium Alloys in Distilled Water: The corrosion resistance of a number of alloys in distilled water was investigated at 95°C. No sample surface preparation was used before or after test. Results are listed in Table V. Because of uncertainty in the rate for unalloyed metal, as previously discussed in connection with Table I, very little can be said as to the effects of the alloying constituents. Harmful additions perhaps include 6% Cb, 2% Ti, 1% Ti plus 2% Zr.

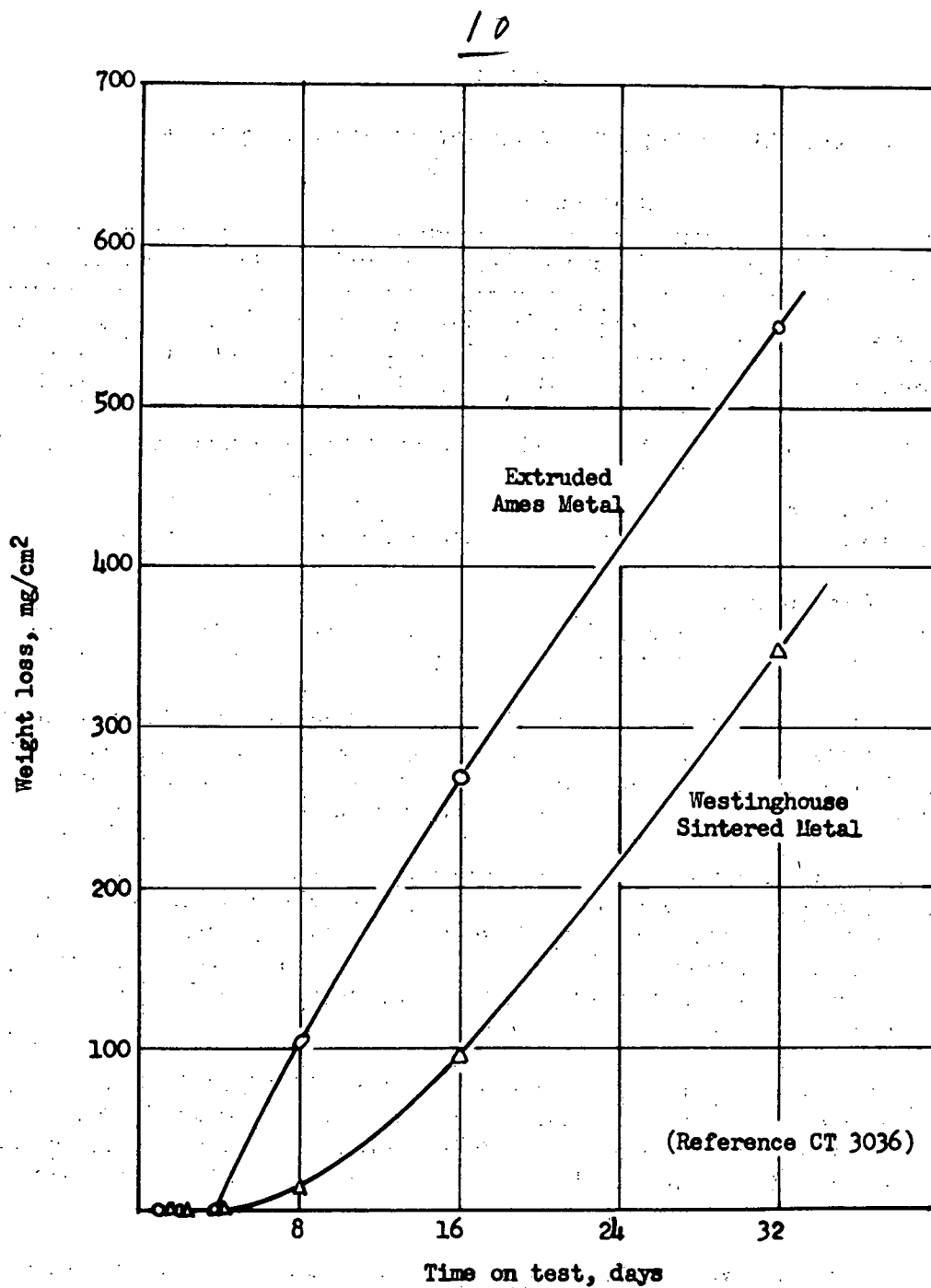


Figure 2

CORROSION OF THORIUM IN DISTILLED WATER
AT 178°C

Table III

CORROSION OF THORIUM AND THORIUM ALLOY
IN FLOW SYSTEM

Simulated Columbia River Water Plus 1 ppm Cl^- and 6×10^{-3} N H_2O_2
at pH 6.5, 70°C, 20-25 ft/sec -- 16 Day Test

(CT-3036)

Metal	Average rate of weight loss from start of test, $\text{mg}/\text{cm}^2/\text{hr}$		
	uncleaned	clean	
<u>Aerated Solution</u>			
A-1 Ames Cast 2 spec.	5.6×10^{-3} 0.3×10^{-3}	10.0×10^{-3} 4.9×10^{-3}	7.5×10^{-3} Avg.
W-1 Westinghouse 2 spec.	2.9×10^{-3} 4.1×10^{-3}	27.0×10^{-3} 18.0×10^{-3}	22.5×10^{-3} Avg.
<u>Hydrogenated Solution</u>			
A-1 Ames cast 2 spec.	0.6×10^{-3} 2.2×10^{-3}	4.9×10^{-3} 8.1×10^{-3}	6.5×10^{-3} Avg.
W-1 Westinghouse 2 spec.	6.2×10^{-3} 12.0×10^{-3}	15.0×10^{-3} 31.0×10^{-3}	23.0×10^{-3} Avg.
<u>Aerated Solution</u>			
Westinghouse sintered + 0.6 wt. % U (3 specimens)			17.5×10^{-3} Avg.

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Table IV

STATIC CORROSION OF THORIUM

Simulated river water plus 1 ppm Cl^- and 1.2×10^{-3} NH_2O_2 , aerated,
pH 7.5, 70°C

Reference: CT-3036

Material	Wt. losses, mg/cm^2	Time, hrs	Average loss from start of test, $\text{mg}/\text{cm}^2/\text{hr}$	
			clean	uncleaned
Ames	13.8	397	170×10^{-3}	80×10^{-3}
Ames	43.7	397	180×10^{-3}	110×10^{-3}
Westinghouse	28.6	397	140×10^{-3}	72×10^{-3}
Westinghouse	62.3	397	200×10^{-3}	157×10^{-3}

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Table V

CORROSION OF THORIUM ALLOYS IN DISTILLED WATER AT 95°C

Test Duration: 30 days

Reference: ORNL-1066

Alloy	Treatment	Average rate of weight change, mg/cm ² /hr, x 10 ³
2% Cr*	1	- 0.096
		- 0.143
4% Cr	1	- 0.290
		- 0.081
2% Cb	1	+ 0.557
		+ 0.101
4% Cb	1	+ 1.393
		+ 0.822
4% Cb	2	- 6.17
		- 3.83
6% Cb	2	-11.35
		-18.62
2% Zr	1	- 3.18
4% Zr	1	- 0.710
		- 0.044
4% Zr	2	- 3.29
		- 3.68
6% Zr	2	- 4.90
		- 5.99
2% Ti	1	+40.6
4% Ti	2	- 7.47
		- 8.68
6% Ti	2	+19.7
		- 0.81
1% Ti, 1% Zr	2	- 3.90
		- 3.49

*By weight

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Table V (Cont'd)

Alloy	Treatment	Average rate of weight change, mg/cm ² /hr, x 10 ³
1% Ti, 2% Zr	2	Disintegrated Disintegrated
2% Ti, 1% Zr	2	-10.90 -10.39
4% ti, 1% Zr	2	- 0.60 - 6.79

Treatments

- (1) Ames metal remelted and cast in ZrO₂ under vacuum cold rolled 68%, and annealed at 750°C for 1 hour in vacuum.
- (2) Ames metal remelted and cast in ZrO₂ under vacuum, cold rolled 75%, and annealed at 750°C for 30 minutes in vacuum.

Of the alloys tested in water at 178°C at another laboratory (Table VI), those which seemed to offer considerably improved corrosion resistance contained small amounts of beryllium or carbon. Of particular interest may be the apparent difference in corrosion between a 1.6% Be alloy melted in graphite and the same alloy melted in beryllia.

Using different mechanical methods of removing the corrosion product, the data in Tables VII and VIII were obtained. Rates of corrosion cannot be estimated with any accuracy, but in several cases alloy corrosion was considerably more severe than that of the parent metal. In no case is it certain that alloying with beryllium improved the corrosion resistance.

The corrosion of beryllium alloys in steam at 100° and 140°C is reported in Table IX. Samples were not cleaned after test: weight changes were divided by the exposure time to give the rates in the last column. The amount of corrosion cannot be deduced well from the data available, but minimum attack seems to have occurred with a relatively small amount of beryllium in the alloy.

Table VI

CORROSION OF THORIUM ALLOYS IN WATER (178°C)

(Autoclave Tests)

Reference: CT-3036

Time in test Alloy	Weight change, mg/cm ² , based on uncleaned specimens						Clean (1) Specimens
	0.8 days	1.7 days	4 days	8 days	16 days	32 days	32 days
Blank (Westinghouse Thorium) (2)	0.47	0.00	- 0.04	- 12.3	- 94.3	-348.	
1.08 w/o Si	0.51	0.69	1.0	- 39.2	-171.	-495.	
2 w/o Si	0.20	0.26	1.0	- 9.3	-106.	-339.	
4.3 w/o Si	0.0	- 0.28	0.03	- 12.3	- 74.	-249.	
0.62 w/o Si + 1.11 w/o Be	- 0.58	- 1.0	- 0.96	- 0.83	- 3.8	+ 0.4	-15.0
0.4 w/o Be	0.46	1.7	1.65	5.0	7.0	+ 28.	- 7.7
0.94 w/o Be	0.32	- 0.13	(3)c. c.	----	----	----	
1.6 w/o Be, melted in graphite	- 0.02	- 0.63	- 0.72	- 1.0	- 0.9	- 0.6	- 9.0
1.6 w/o Be, melted in BeO	- 0.36	- 0.23	3.4	c. c.	----	----	
2.46 w/o Be	- 0.55	- 1.2	- 1.1	- 0.97	- 0.6	- 0.7	-46.
2.02 w/o Cb	- 4.6	- 18.	- 59.3	-153.5	-328.	-673.	
4.17 w/o Cb	-73.	-179.	-503.	c. c.	----	----	
2.75 w/o Fe	0.25	- 45.6	-114.	-242.	-573.	c. c.	
5.53 w/o Fe	0.50	1.1	- 0.87	- 1.7	-255.	c. c.	
0.3 w/o C	- 0.09	- 0.4	- 0.16	- 0.69	- 0.4	- 0.7	-11.0
1.24 w/o C	0.0	c. c.					
0.6 w/o U	----	19.0	c. c.				

(1) Cleaned with 70% HNO₃ plus 0.1% NaF at 115°C.

(2) Ingot analyzed 300 ppm Be at top and 20 ppm Be at bottom. Corrosion specimen taken from middle of ingot.

(3) c. c. means specimen was completely corroded.

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Table VII

CORROSION OF THORIUM AND THORIUM-BERYLLIUM ALLOYS
IN WATER AT 100°C

Reference: CT-2715

Composition, % Be	Length of test, hrs	Average rate of weight gain, mg/cm ² /hr, x 10 ³			
		Method 1	Method 2	Method 3	Method 4
0	90	+1.03	- 1.71	-3.09	-22.3
0.5	90	+ .85	- 1.13	-1.97	-44.0
1.0	91	-	+11.10	+1.72	-88.0
2.0	91	No change	zero	zero	-56.8

Methods:

- 1: Sample removed, washed, dried, and weighed.
- 2: Sample, when dried, brushed off with camel's hair brush and weighed.
- 3: Sample polished on wheel fitted with non-metal-cutting wool cloth (AB. Miracloth) and weighed.
- 4: Sample polished to bright metallic luster on wheel fitted with 000 emery polishing paper and weighed.

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Table VIII

CORROSION OF THORIUM AND THORIUM-BERYLLIUM ALLOYS
IN WATER

Reference: CT-2715

Composition, % Be	Length of test, hrs	Average rate of weight gain, mg/cm ² /hr, x 10 ³			
		Method 1	Method 2	Method 3	Method 4
		<u>at 140°C</u>			
0	138	+ 1.64	- 0.99	- 2.52	- 48.9
0.5	138	-747.	-787.	-817.	-1110.
1.0	138	+ 5.45	+ 3.89	+ 1.17	- 106.
2.0	138	+ 10.73	+ 9.1	+ 7.68	- 66.
		<u>at 180°C</u>			
0	71	+ 2.34	- 7.04	- 8.98	- 68.7
2.0	70	-	-	- 95.2	- 415.

Methods:

- 1: Sample removed, washed, dried, and weighed.
- 2: Sample, when dried, brushed off with camel's hair brush and weighed.
- 3: Sample polished on wheel fitted with non-metal-cutting wood cloth (AB Miracloth) and weighed.
- 4: Sample polished to bright metallic luster on wheel fitted with 000 emery polishing paper and weighed.

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Table IX

CORROSION OF THORIUM-BERYLLIUM ALLOYS IN STEAM

Reference: CS-2614

Wt % Be	Time, hours	Wt. change, mg/cm ² /hr, x 10 ³
<u>At 100°C, 1 atmosphere pressure</u>		
0.0	193	+ 1.365
0.519	214	- 0.583
1.033	214	- 0.066
1.80	216	+ 0.081
3.04	225	+ 0.282
3.59	214	+ 0.322
<u>At 149°C, ca. 30 psig</u>		
0	64	+ 0.508
0.519	64	+ 0.197
1.033	64	+ 0.329
1.80	64	+ 0.404
3.04	64	+ 0.364
3.59	64	+ 0.260

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Beryllium Alloy in Various Solutions: An alloy containing 0.5 w/o Be was tested in nitrates and nitric acid, as shown in Table X. The alloy, made with Ames metal, lost weight at a rate of 5 to 7 times that in water for the more dilute solutions, dissolving much more rapidly in concentrated nitric acid.

Discussion

Information available is insufficient to draw conclusions as to the essential features which influence the corrosion behavior of thorium. A definite increase in aqueous corrosion rate is shown when the temperature is increased from 100° to 178°C.

It is possible that the wide variation in corrosion behavior observed for different metal samples has been due chiefly to the oxygen and/or carbon content of the metal. The Ames metal used was characteristically much higher in carbon and lower in oxygen than the Westinghouse metal. Analytical difficulties have been considerable, and the content of these elements has not been known accurately.

Further evidence concerning the point is the reduction in metal corrosion caused by the addition of small amounts of beryllium and carbon, elements with a high affinity for oxygen. Evidence is too scanty to conclude whether the effect of carbon is simply to reduce the oxygen content of the metal, although the loss of corrosion resistance caused by further carbon addition suggests that the presence of carbon is not particularly desirable. Careful preparation of metal specimens of known composition would allow clarification of this point.

The dependence of corrosion on cold work reported in Table I might have been due to the amount of oxygen worked into the surface metal, or the oxidation that took place during the annealing operations. The fact that no surface metal was removed before the single exposure to distilled water leads to the belief that no conclusions should be drawn about comparative results of the test. Surface oxidation before test does influence the corrosion observed; for example, anodic pretreatment has been reported as reducing the attack by water (CT-3054). Such behavior is perhaps only temporary, and long tests, with periodic weighing, might give much more reproducible results. Even under most favorable testing procedures, only one exposure time can give misleading results. If an eight-day test had been run for the samples whose behavior was given by the top curve in Figure 1, "rates" determined would have been larger than the slope of the linear portion of the curve by a factor of seven or so; if the test had been for 24 days, such a "rate" would have been double the slope of the curve.

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Table X

CORROSION OF Th/0.5 w/o Be ALLOY IN VARIOUS SOLUTIONS

Reference: CT-2715

Solution	Temp, °C	Time of test, hrs	Average rate of weight loss mg/cm ² /hr
0.3 M Uranyl) nitrate)	100	114	0.0655
0.1 M HNO ₃)			
0.3 M Thorium nitrate	100	114	0.0414
0.5 M Nitric acid	98	113	0.0483
Concentrated) (15.4 M)) Nitric acid)	86	113	1.235

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The "induction period" of only slight corrosion during the initial part of the exposure is characteristic of fairly good quality metal. The cause of the phenomenon is not known, although it was presumed to have been caused by a protective surface layer, probably oxide produced by contact with air before test. The same behavior was exhibited when supposedly clean samples were exposed to purified hydrogen at 400°C (CT-3045).

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APPENDIX: ABSTRACTS FOR REACTION WITH GASES

Air

CT-2400: Ames cast thorium gained weight linearly with time after various induction periods at temperatures from 300 to 500°C. Rates are given very roughly by the equation:

$$\log G = 9.25 - \frac{6250}{T} \quad (G \text{ in mg/cm}^2/\text{hr}; T, \text{ degrees Kelvin})$$

A 2 w/o beryllium alloy showed essentially the same behavior from 400 through 450°C, following the equation

$$\log G = 5.55 - \frac{3910}{T} \quad (G \text{ in mg/cm}^2/\text{hr}; T, \text{ degrees Kelvin})$$

At 500°C, however, its rate of weight gain decreased after about 2 hours. The slope of the curve (straight line) subsequent to that time was too low to fit the log G equation above.

ME-110: Penetration rates for the oxidation of thorium in still air were 0.5, 15, 18 mm/year at 100, 200, 300°C, respectively.

CT-2093: Air scaling rates given for 300-900°C, and the effect of air velocity. For Ames and Westinghouse metal. Weight gains after 1/2 hour in several gases at 800°C were as follows:

Air	6.0 g/cm ² gain
Tank N ₂	4.4
Purified N ₂	2.0
Tank A	1.0
Purified A	0.75

23Hydrogen

CT-3054: Equilibrium vapor pressure of hydrogen over thorium hydride, analyzed as $\text{ThH}_{3.2}$ is given by the equation:

$$\log P = 7.50 - \frac{2800}{T} \quad (P \text{ in mm Hg; } T, \text{ degrees K}).$$

CT-3045: After induction periods for freshly ground surfaces, depending on temperature, the linear absorption of hydrogen proceeded at the following rates, assuming the reaction product to be ThH_4 :

Temperature °C	Rate, mg Th/cm ² /hr		
	Westinghouse Metal	Ames Metal	Hot-wire Metal
505	129		174
475	109		
440	88.4		
425	84.5		
400	80	168	
180	19.7	23.6	
100	14.6		

The product took several days to be converted to ThO_2 by water at 178°C (See also CT-3036).

CS-2672: Reaction $\text{Th} + \text{H}_2$ is strongly exothermic, X-ray diagrams indicate formation of at least two hydride phases. Both phases and finely divided metal are pyrophoric.

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