ORNL 1066
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THORIUM AND THORIUM ALLOYS

PRELIMINARY CORROSION TESTS

OAK RIDGE NATIONAL LABORATORY • U.S. ATOMIC ENERGY COMMISSION

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REACTOR EXPERIMENTAL ENGINEERING DIVISION

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Arnold R. Olsen

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ABSTRACT

The corrosion resistance of thorium and thorium alloys containing from 2 to 6% chromium, columbinium (niobium), titanium, zirconium and titanium-zirconium in distilled water at 95°C has been investigated.

The true effects of the various alloy additions could not be determined because of the more marked effect of cold working. It was found that a sample cold rolled 75% and annealed would show a tenfold higher weight change over an otherwise identical sample cold rolled 68% and annealed; or a decided loss in weight compared to a relatively small gain.

It is planned to investigate this phenomenon further.

INTRODUCTION

The Metallurgy Division of ORNL is engaged in a thorium research program which includes alloy development work. Since corrosion characteristics can be an important factor in determining the application of thorium and/or its alloys, the Corrosion Group of the Reactor Experimental Engineering Division was asked to make corrosion tests on samples of the various alloys.

As there was no specific application in mind and in view of the common usage of water as a coolant, this was chosen as the medium. A temperature of 95°C was chosen because it permitted use of testing equipment already available in the corrosion laboratory and it represents a practical maximum for the use of water under atmospheric pressure. It has been found in the past that an exposure period of one month is long enough to indicate those materials which have no possible application because of excessive corrosion, and yet tests of this length do not involve excessive manpower.

TEST CONDITIONS

As was stated in the introduction, the corrosion conditions were chosen rather arbitrarily.

Corrosion Medium

Distilled water of the typical analysis listed in Table I, Column 1 was used as the medium. The water was not changed during the entire exposure period nor was any attempt made to control the pH. Column 2 of Table I is an analysis of the water made after the test period. The temperature was maintained at $95 \pm 1^{o}C$.

Test Apparatus

The tests were conducted by individually suspending the samples from pyrex glass hooks totally submerged in a battery jar containing 16 liters of distilled water. The solution temperature was maintained by an electrically heated water bath. Excessive evaporation loss was avoided by the use of 2S aluminum plate covers on the battery jar.

Sample Composition, Preparation and Treatment

All samples were tested as received from the Metallurgy Division. No mechanical working or etching was done by the corrosion group. Samples were degreased in acetone and alcohol, dried and weighed.

Sample identification, alloy composition and metallurgical history is listed in Table II.

After testing, samples were dried, weighed and examined visually. Originally the intention was to examine defilming techniques and base the rate of attack on defilmed weights. The gross differences between samples and the high rate of attack made this procedure unnecessary. Consequently the weight changes are as removed from the testing medium.

TABLE I

CORROSION MEDIUM ANALYSIS
(Distilled Water)

Concentration of all Constituents in Sample	1 Before	2 After	Units
pH	5.55	5.0	
Ppn. Alkalinity as $CaCO_3$	0.0	0.0	ppm
M.O. Alkalinity as $CaCO_3$	2.1	2.0	ppm
Specific Resistance	2.75×10^5	1.5×10^5	ohms-cm
Soap Hardness as $CaCO_3$ detn.	8.3	8.0	ppm
Dissolved CO_2	1.0	1.0	
Dissolved Solids	5.8	6.1	
Non-Volatile Solids	2.2	3.3	
SiO_2	0.5	0.5	
Fe	.02	.02	
Al	0.05	.06	
Cu	0.02	.02	
Ni	0.02	.02	
Cr	0.02	.02	
U	-	-	
Ca	1.9	1.9	
Mg	0.1	.1	
Na	1.7	1.7	
SO_4	4.0	4.1	
Cl	0.1	1.9	
CO_3	1.2	1.2	
HCO_3	2.3	2.4	
NO_3	0.8	0.7	
PO_4	0.3	0.3	
F	0.02	.02	

TABLE II

SAMPLE IDENTIFICATION, COMPOSITION AND METALLURGICAL TREATMENT

Sample Number	Code* Number	Composition	Treatment
1	Ames W	Th	
2	Ames C	Th	Cold rolled 75% and annealed at 750°C for 30 minutes in vacuum
3	Ames W	Th	Cold rolled 86% and annealed at 750°C for 30 minutes in vacuum
4	Ames W	Th	Cold rolled 86%
5	Ames W	Th	Cold rolled 25%
6	No. 3	Th	Ames W remelted and cast in ZrO_2 under Argon, cold rolled 68%, annealed at 750°C for one hour in vacuum
7	A592	Th	Ames metal remelted and cast in ZrO_2 under vacuum, hot rolled 80%, cold rolled 40% and annealed at 750°C for one hour in vacuum
8	A472	Th-2% Cr	Ames metal remelted and cast in ZrO_2 under vacuum, cold rolled 68% and annealed at 750°C for one hour in vacuum
9	A487	Th-4% Cr	Same as (8)
10	A425	Th-2% Cb	Same as (8)
11	A424	Th-4% Cb	Same as (8)
12	A625	Th-4% Cb	Ames metal remelted and cast in ZrO_2 under vacuum, cold rolled 75% and annealed at 750°C for 30 minutes in vacuum
13	A627	Th-6% Cb	Same as (12)
14	A429	Th-2% Zr	Same as (8)
15	A417	Th-4% Zr	Same as (8)

TABLE II (CONT'D)

SAMPLE IDENTIFICATION, COMPOSITION AND MDETALLURGICAL TREATMENT

Sample Number	Code* Number	Composition	Treatment
16	A613	Th-4% Zr	Same as (12)
17	A614	Th-6% Zr	Same as (12)
18	A433	Th-2% Ti	Same as (8)
19	A621	Th-4% Ti	Same as (12)
20	A624	Th-6% Ti	Same as (12)
21	A615	Th-1% Ti-1% Zr	Same as (12)
22	A616	Th-1% Ti-2% Zr	Same as (12)
23	A619	Th-2% Ti-1% Zr	Same as (12)
24	A620	Th-4% Ti-1% Zr	Same as (12)

*Ames C - Late shipment of Ames cast metal

Ames W - Early Ames production, rolled at Westinghouse, annealed, cold rolled 68% and annealed one hour at 750°C in vacuum

All other numbers are ORNL Metallurgy Division melt numbers

TEST RESULTS

The results of the thirty-day exposure to distilled water at 95°C are listed in Table 3 together with a brief description of sample appearance at the end of the test. These descriptions may be compared with the photographs in Figures 1 through 11.

TABLE III

CORROSION RATES OF THORIUM AND THORIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS

Sample	Test No.	Wt. Change MDM*	Appearance
1	153	-31.9	Dull gray-white, loosely adherent powder
1	153A	-26.6	Same
2	169	-590	Mottled dark gray on gray-white - sluffing
2	169A	-609	Same
3	170	-1,850	Mottled dark gray on gray-white - sluffing. Also severe pitting attack
3	170A	-1,190	Same
4	171	-518	Sample black - exfoliated along rolling plane
4	171A	-430	Same
5	154	-15.9	Dull gray-white, loosely adherent powder - incipient cracks
5	154A	-23.7	Same
6	155	-11.2	Same
6	155A	- 7.1	Same
7	172	-720	Mottled black on gray-white - sluffing - marked pitting attack
7	172A	-576	Same
8	157	- 6.9	Gray-white, loosely adherent powder - some flaking
8	157A	-10.3	Same
9	158	-20.9	Dull gray - fairly adherent powder
9	158A	- 5.8	Same
10	156	+40.1	Mottled dark gray, loosely adherent powder - some flaking
10	156A	+ 7.3	Same

TABLE III (CONT'D)

CORROSION RATES OF THORIUM AND THORIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS

Sample	Test No.	Wt. Change MDM*	Appearance
11	160	+100.3	Spotted dark gray and black, loose powder - some flaking
11	160A	+ 59.2	Same
12	181	-444	Light gray sluffing scale - some pitted with what looks like erosion
12	181A	-276	Same
13	182	-817	Black, exfoliated and flaking badly
13	182A	-1,341	Same
14	161	-229	Light gray, loosely adherent powder
15	162	- 51.1	Light gray, loosely adherent powder
15	162A	- 3.2	Same
16	173	-237	Gray-white, loosely adherent powder
16	173A	-265	Gray-white, loosely adherent powder, cracked
17	174	-353	Dark gray powder - sluffing
17	174A	-431	Same
18	159	+2,926	Dark gray - blistered and exfoliating
19	179	-538	Gray - slightly blistered - flaking badly
19	179A	-625	Same
20	180	+1,420	Same
20	180A	- 58	Same
21	175	-281	Light gray powder - sluffing
21	175A	-251	Same
22	176	-	Sample totally disintegrated
22	176A	-	Same
23	177	-785	Light gray, spotted, yellowish-brown - pitted
23	177A	-748	Same
24	178	- 43	Black on gray - appearance of erosion - flaking
24	178A	-488	Same

*MDM - Milligrams per square decimeter per month

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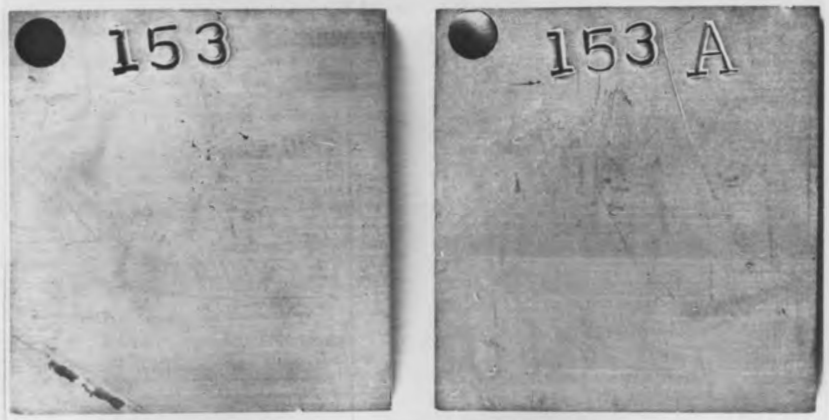
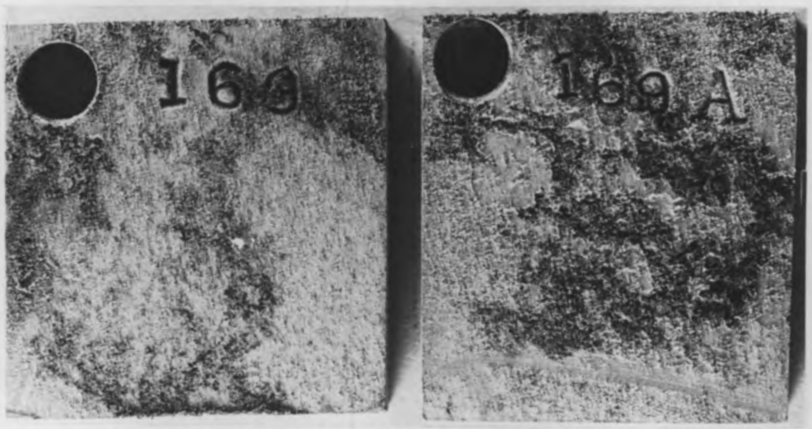
PHOTO NO. 10768



SAMPLE NO. 1 (68% C.R.)



SAMPLE NO. 2 (75% C.R.)

SAMPLE NO. 3 (86% C.R.)

FIGURE I. AMES THORIUM COLD ROLLED AND ANNEALED SHOWING CORROSION ATTACK AFTER 30 DAYS EXPOSURE TO DISTILLED WATER AT 95°C.

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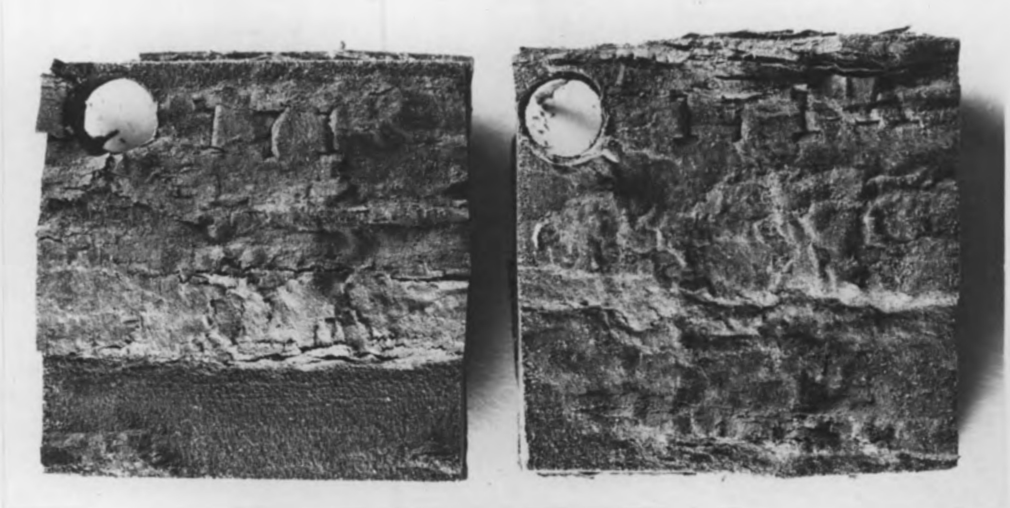
PHOTO NO. 10769



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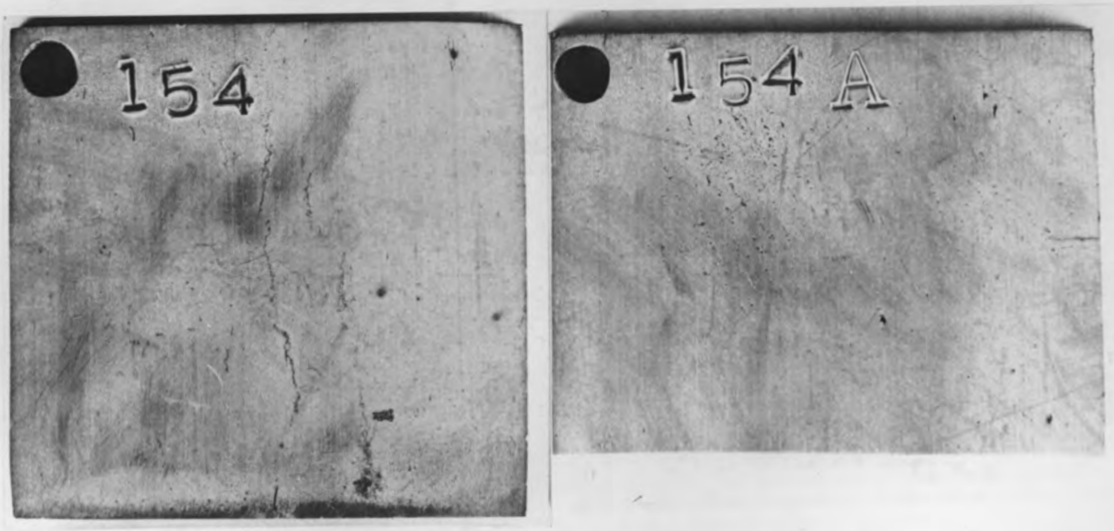

SAMPLE NO. 5 (25% C.R)

FIGURE 2. CORROSION OF AMES THORIUM IN THE COLD ROLLED CONDITION BY DISTILLED WATER AT 95° FOR 30 DAYS.

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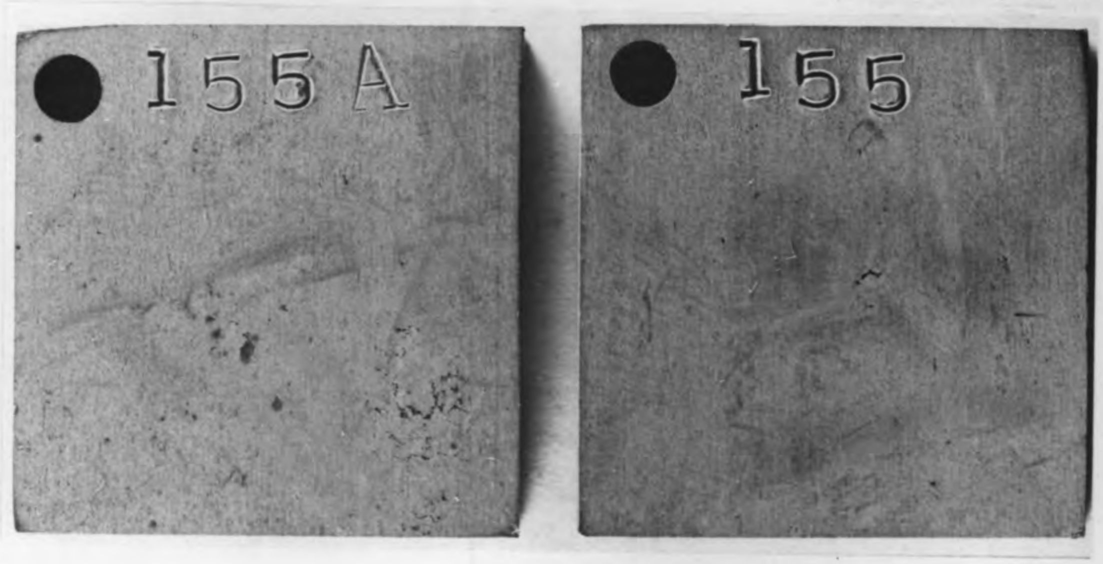
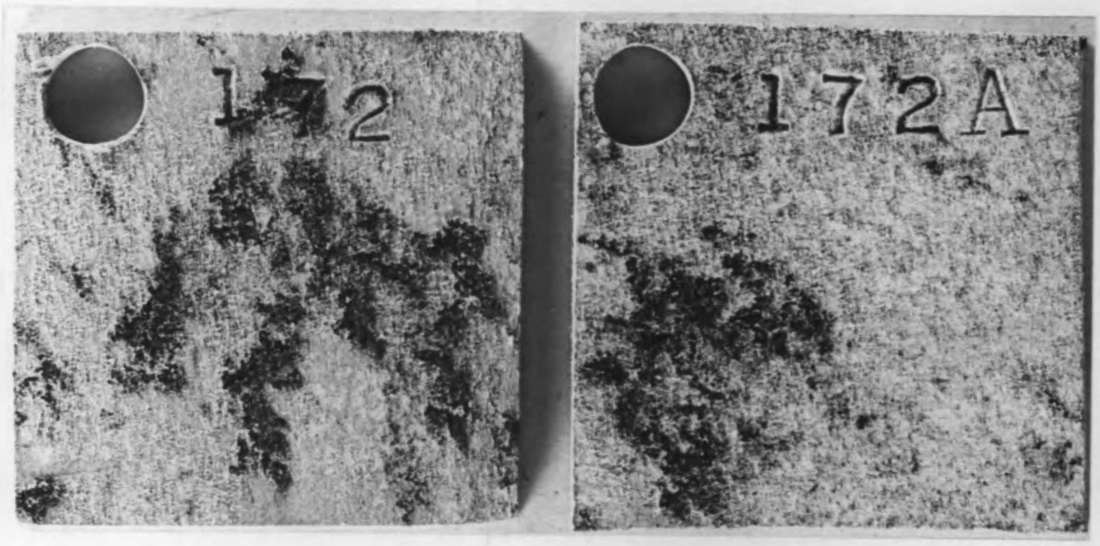
PHOTO. NO. 10770



SAMPLE NO. 6.



SAMPLE NO. 7.

FIGURE 3. CORROSION OF REMELTED THORIUM IN THE ANNEALED CONDITION AFTER EXPOSURE TO DISTILLED WATER AT 95° FOR 30 DAYS.

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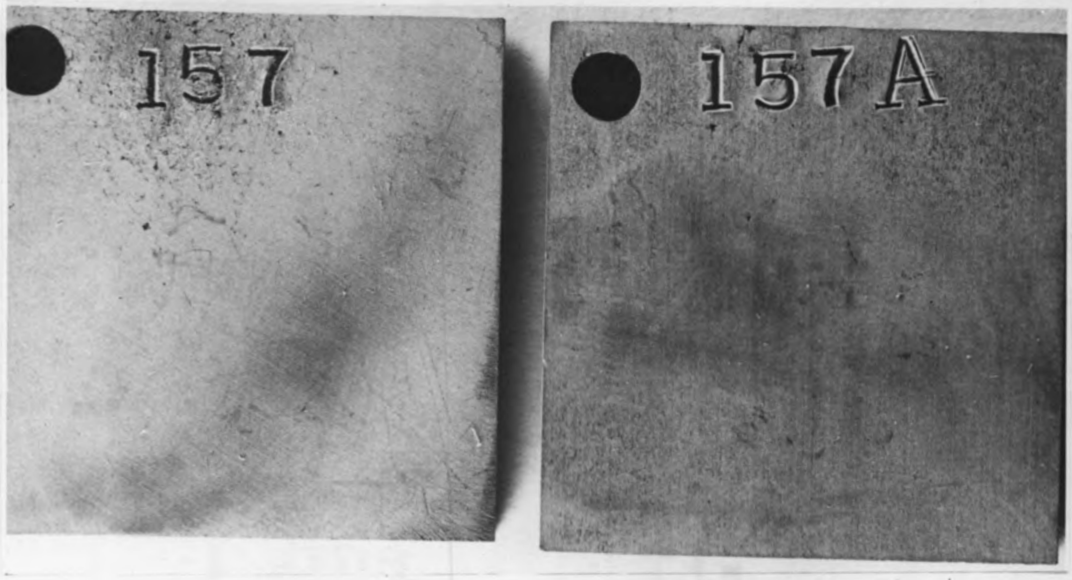
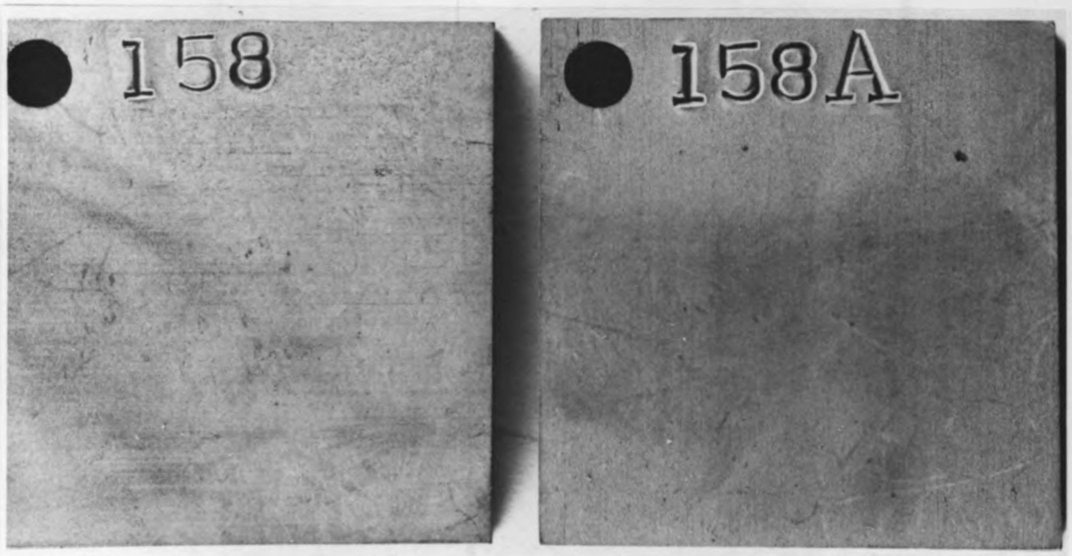
PHOTO NO. 10771



SAMPLE NO. 8 (2% C. R.)



SAMPLE NO. 9 (4% C.R.)

FIGURE 4. CORROSION OF THORIUM — CHROMIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95° FOR 30 DAYS.

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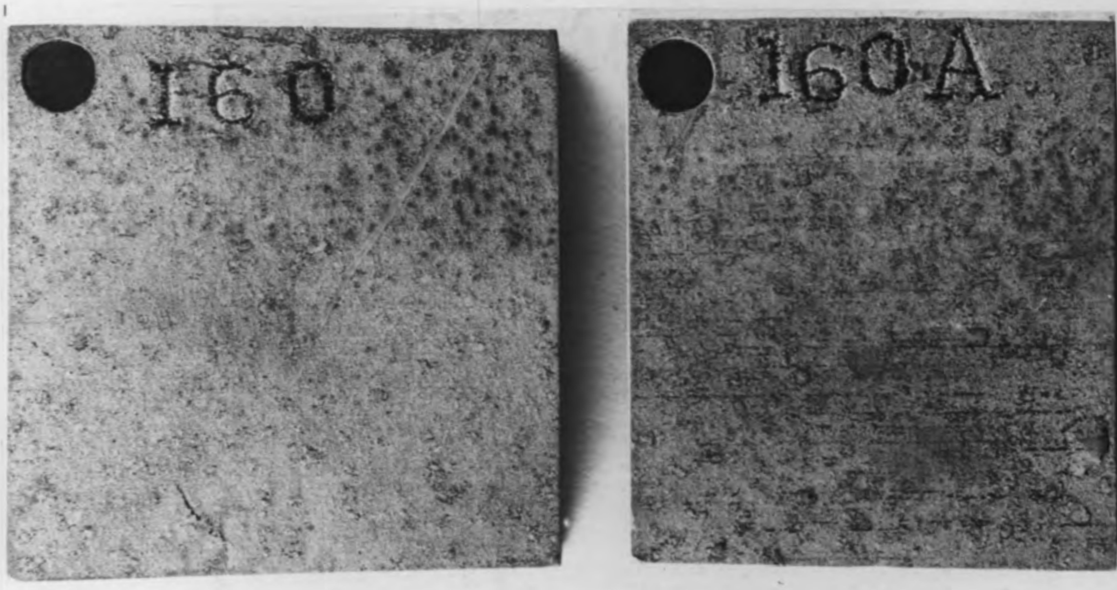
PHOTO NO. 10772

SAMPLE NO.10 (2% Cb)



SAMPLE NO.11 (4% Cb–68% C.R.)

FIGURE 5. CORROSION OF THORIUM–NIOBIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

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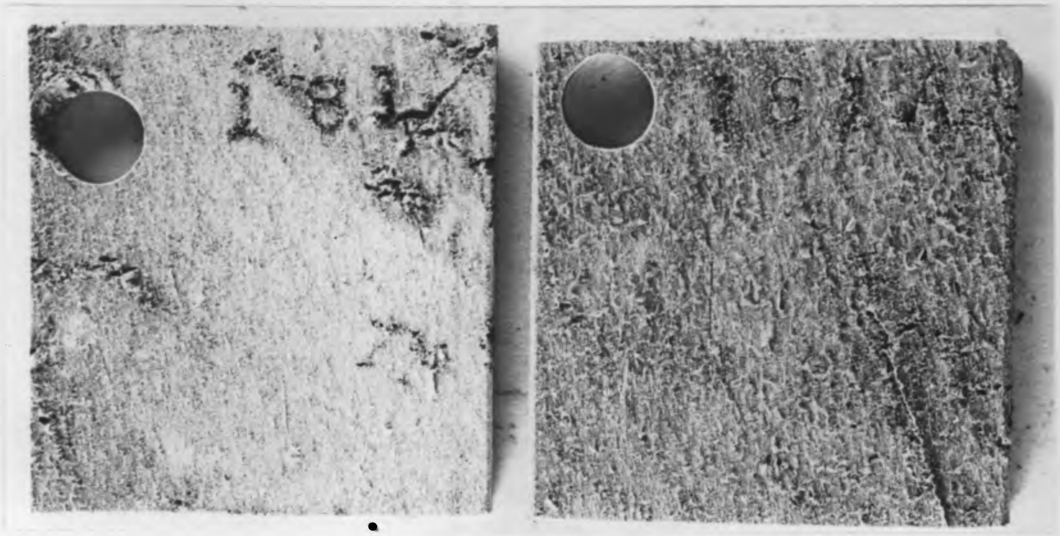
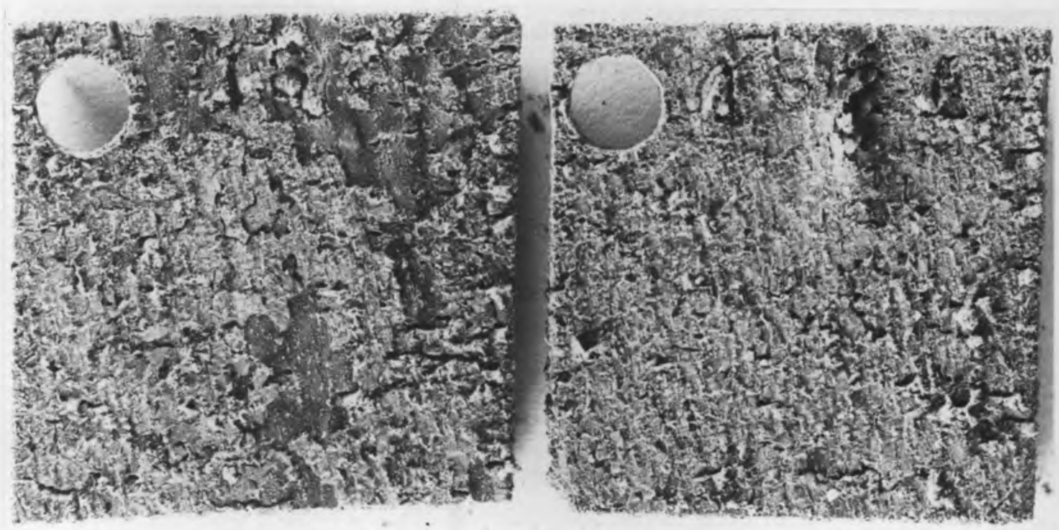
PHOTO NO.10773



SAMPLE NO. 12 (4% Cb-75% C.R).



SAMPLE NO.13 (6% Cb)

FIGURE 6. CORROSION OF THORIUM-NIOBIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95° C FOR 30 DAYS.

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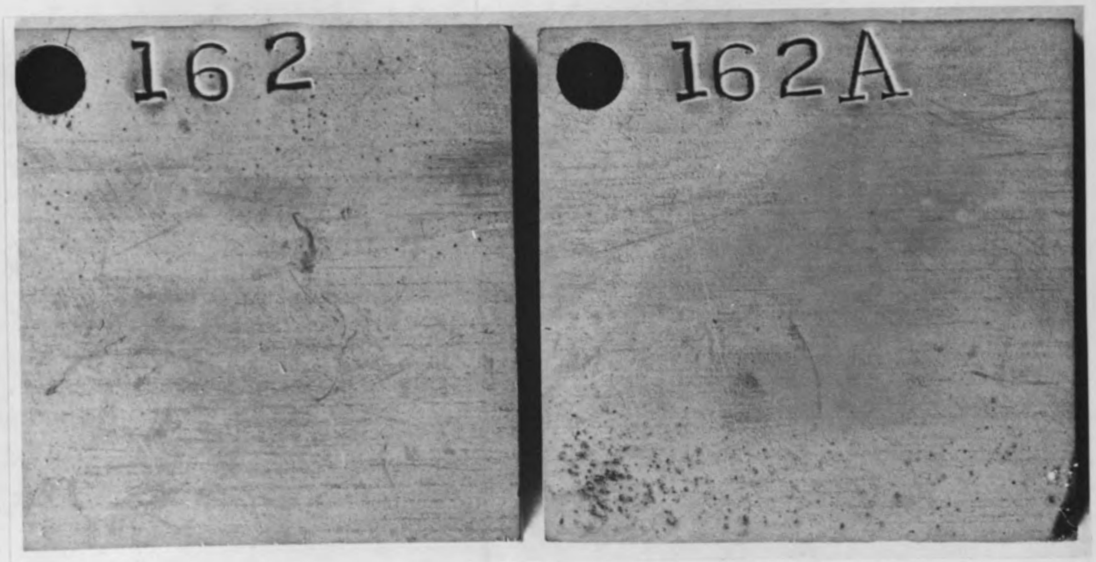
PHOTO NO. 10774

SAMPLE NO.14 (2% Zr)



SAMPLE NO.15 (4% Zr-68% C.R.)

FIGURE 7. CORROSION OF THORIUM-ZIRCONIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

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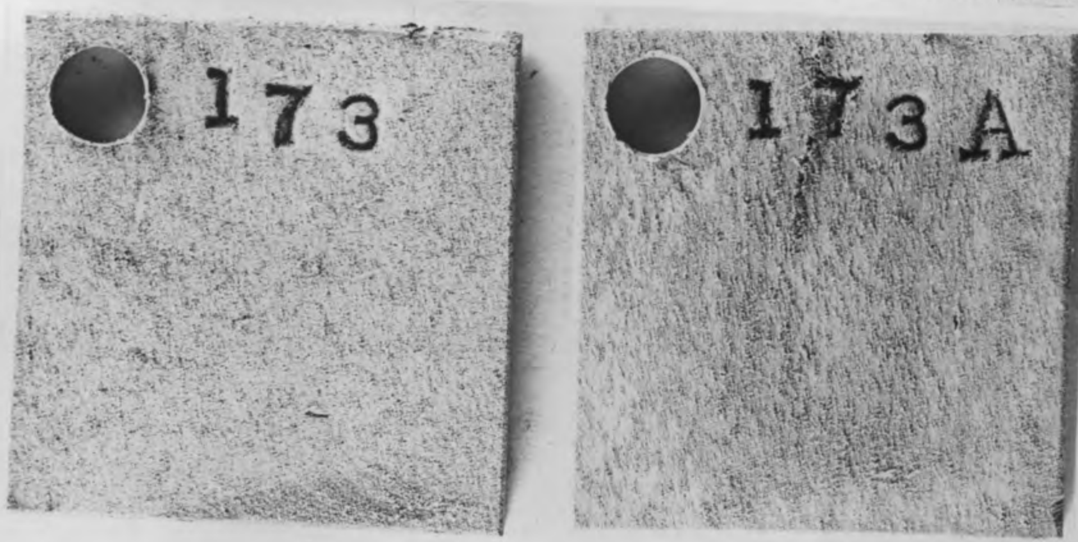
PHOTO NO. 10775



SAMPLE NO. 16 (4% Zr-75° C.R.)

SAMPLE NO. 17 (6% Zr)

FIGURE 8. CORROSION OF THORIUM—ZIRCONIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

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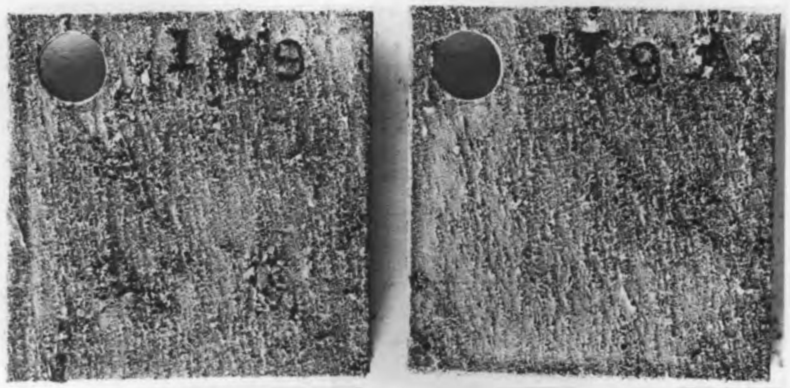
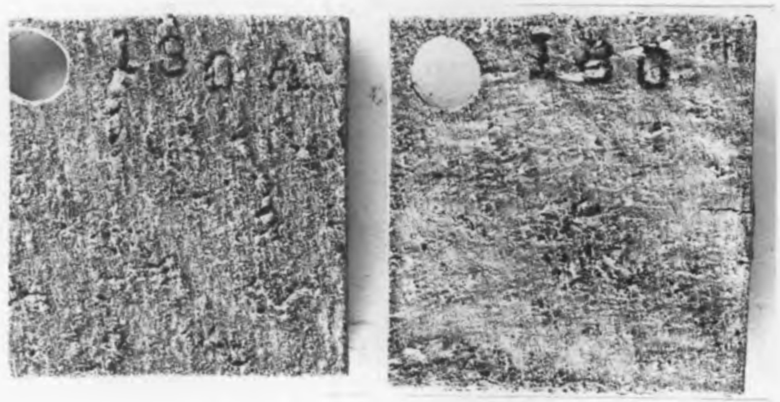
PHOTO NO. 10776

SAMPLE NO. 18 (2% Ti)



SAMPLE NO. 19 (4% Ti)



SAMPLE NO. 20 (6% Ti)

FIGURE 9. CORROSION OF THORIUM-TITANIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

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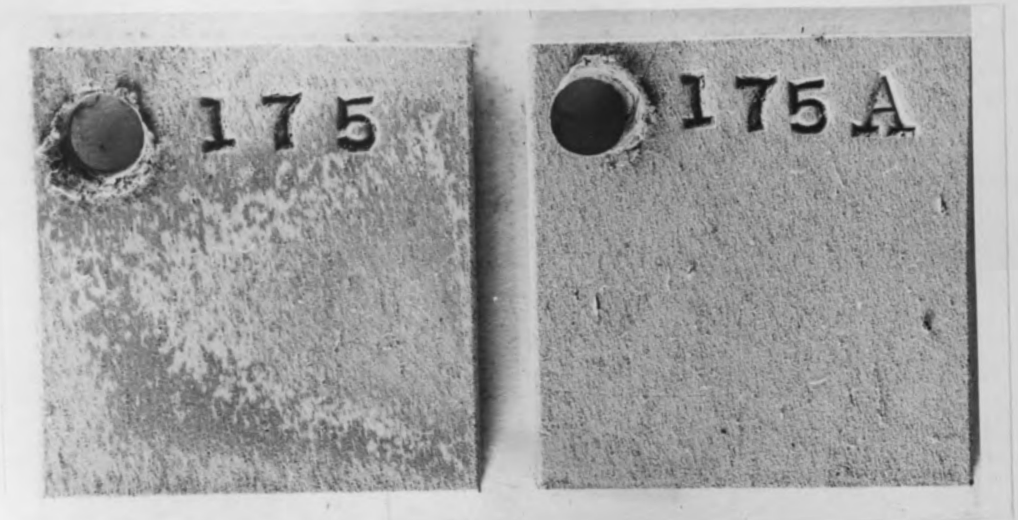
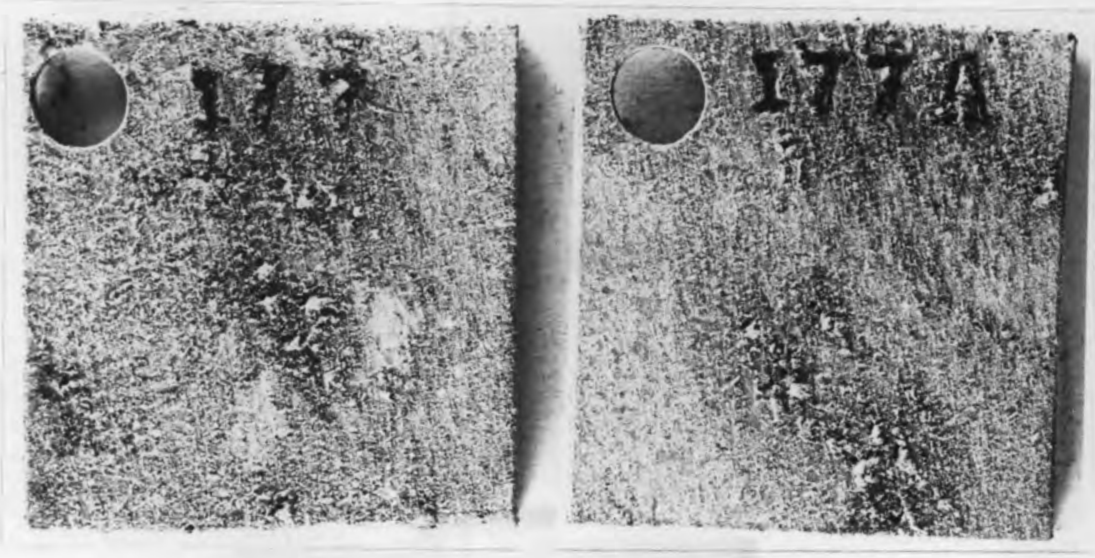


SAMPLE NO. 21 (1% Ti – 1% Zr)

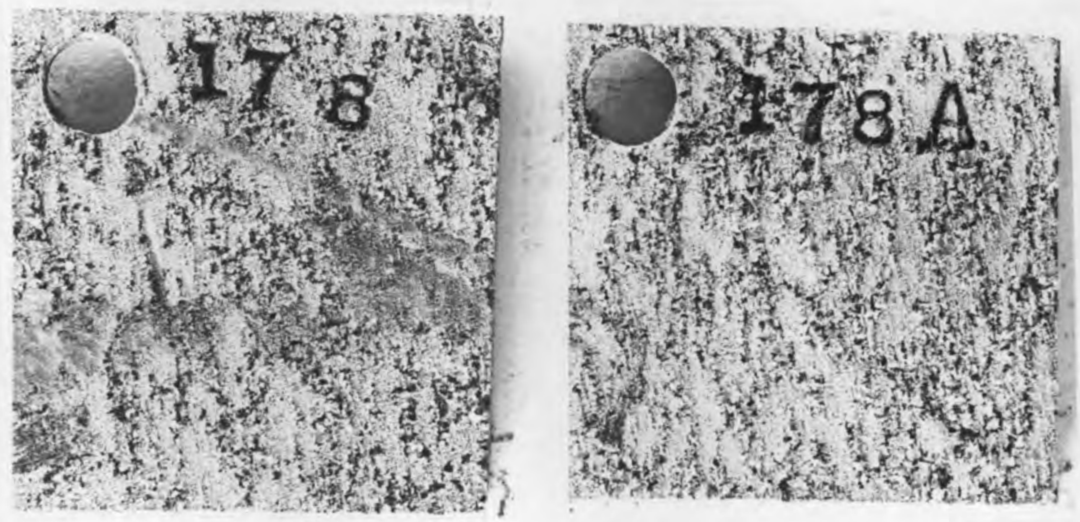
SAMPLE NO. 22 (1% Ti – 2% Zr)

FIGURE 10. CORROSION THORIUM-TITANIUM-ZIRCOIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

PHOTO NO. 10778



SAMPLE NO. 23 (2% Ti-1% Zr)



SAMPLE NO. 24 (4% Ti-1% Zr)

FIGURE 11. CORROSION OF THORIUM-TITANIUM-ZIRCONIUM ALLOYS EXPOSED TO DISTILLED WATER AT 95°C FOR 30 DAYS.

DISCUSSION OF TEST RESULTS AND PLANNED TESTS

The large weight changes and the obvious attack of the samples explains the elimination of the investigation of defilming techniques at this time.

However, the marked difference in rate of attack caused by relatively small differences in cold working has raised a question requiring further investigation. Corrosion attack shown in Figure 1 with three degrees of cold rolling prior to annealing, backed up by the results shown in Figure 3 for remelted stock, Figures 5 and 6 on a 4% niobium alloy and Figures 7 and 8 on a 4% zirconium alloy, indicate that corrosion-wise the amount of cold working, despite subsequent annealing, has more effect than many of the alloy additions.

Consequently, a set of samples is being prepared to investigate further this phenomenon in the hope of determining the reason for the change, and possibly finding a lead to improving the corrosion resistance of all thorium.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the following people for their cooperation and assistance in making these tests.

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