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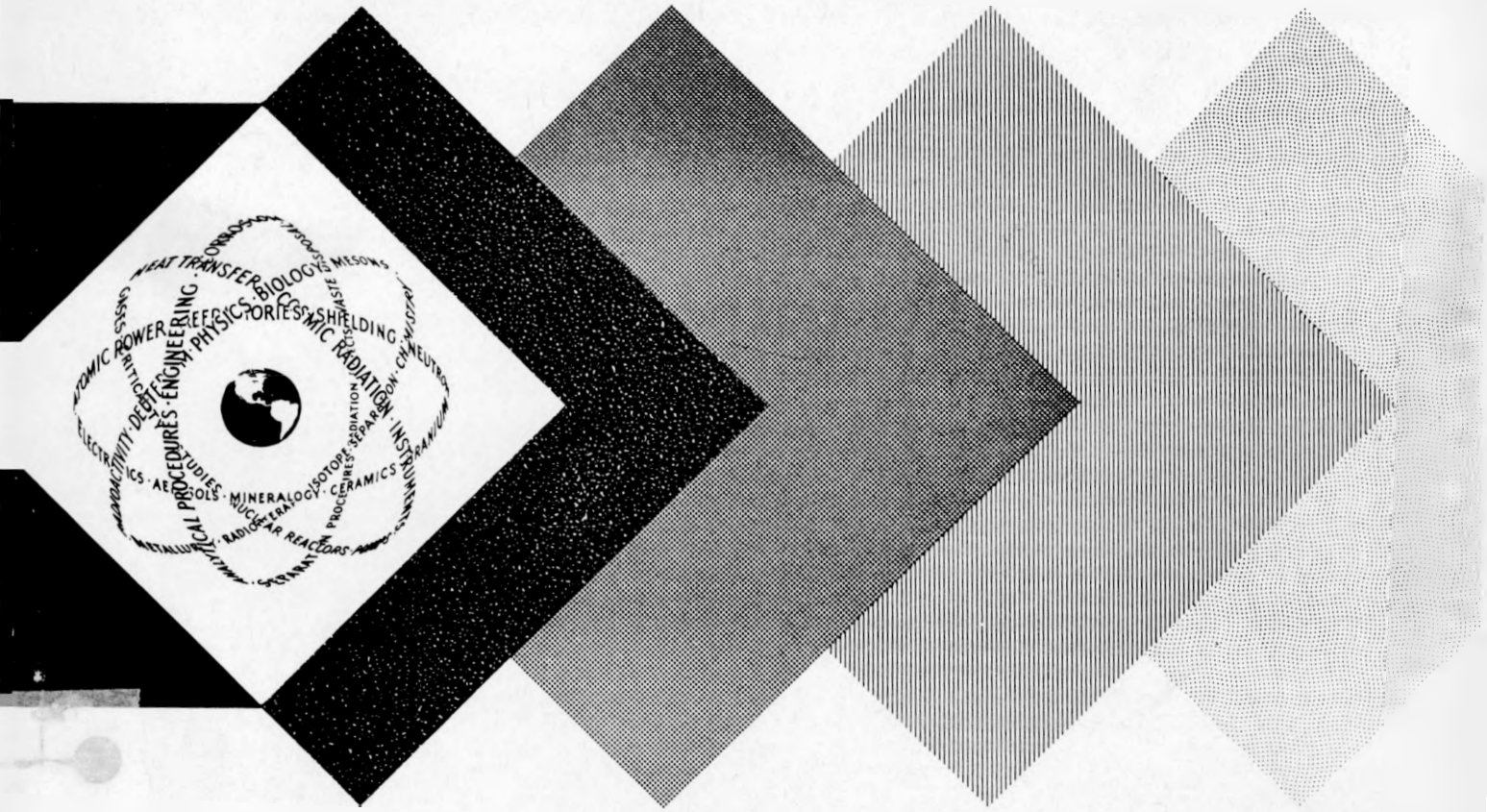
AQUEOUS CORROSION OF THORIUM ALLOYS AND ZIRCALOY-CLAD THORIUM ALLOYS

By
D. S. Kneppel

March 22, 1960

Nuclear Metals, Inc.
Concord, Massachusetts



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D. S. Kneppel

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Nuclear Metals, Inc.
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A. R. Kaufmann
Technical Director

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ABSTRACT

An investigation was made of the ability of thorium alloys extrusion-clad with Zircaloy-2 to survive catastrophic rupture when the core alloy was exposed to high temperature water through a small artificial defect in the cladding. At the same time the aqueous corrosion resistance of various thorium alloys was determined at a series of temperatures, and their activation energies were obtained. Thorium-zirconium alloys containing 5-10 $^{w}/_{o}$ Zr showed the lowest corrosion rate, 25 $mg/cm^2/hr$, as compared to 150 $mg/cm^2/hr$ for unalloyed thorium in 500°F water. Defected specimens of Zircaloy-2 clad unalloyed thorium failed catastrophically after a few hours exposure to 500°F water, whereas a thorium core alloy containing 8.8% Zr showed only slight cracking of the clad near the defect after 132 hours exposure. The attack of the core alloy through the defect in the clad appeared to progress, in part, preferentially along the clad-core interface. Heat treatment of the clad alloys to form a diffusion layer between the clad and core was not successful in preventing the attack along the interface. All additions of 10% of uranium to Th - 2% Zr confined the attack to the area just beneath the defect in the clad but resulted in only a slight increase in survival time over the binary Th - 2% Zr alloy.

I. INTRODUCTION

Thorium has been considered as a possible fuel for water-cooled nuclear reactors, but to confine the fission products and protect the fuel from the corrosive effects of the high temperature coolant water, cladding of the thorium with a corrosion-resistant material such as Zircaloy-2 is essential. If complete integrity of the clad could be assured, the corrosion resistance of the thorium would be of no concern, but for safety considerations it must be assumed that accidental exposure of the thorium to high temperature water could occur; an evaluation of the consequent corrosion is therefore desirable. One of the primary objectives of this investigation was the attempt to develop a thorium alloy which, when clad by extrusion with Zircaloy-2, would not show catastrophic failure in high temperature water as a result of a small artificial defect in the cladding. In conjunction with this, the corrosion resistance of a number of thorium alloys was studied, since the consequences of core exposure can be expected to bear a relationship to the core's corrosion resistance.

A literature search showed almost no data available on the corrosion resistance of thorium alloys in water at temperatures above 400°F. S. Isserow[1] investigated the corrosion resistance of Zircaloy-clad thorium and thorium-carbon alloys in 500 and 650°F water. He found that thorium alloys tested in 500°F water had a corrosion rate 6 times lower than unalloyed thorium. However, since cladding of the thorium alloy would be essential in a water-cooled reactor, it is useful to assess the alloy's ability to survive catastrophic failure caused by accidental exposure of the core alloy through a break in the cladding. Previous work[1] at this laboratory did not succeed in preventing rapid corrosion and rupture of artificially defected, extrusion-clad thorium specimens. Failure invariably occurred in less than 24 hours in 500°F water. The present work with thorium alloys was successful to the extent that the life of defected clad samples was extended to over 100 hours in 500°F water.

The investigation consisted of two separate phases. The first phase, a study of the corrosion resistance of thorium alloys prepared by arc melting, was also used to screen the alloys for the second phase of the investi-

gation. The second phase was the study of the corrosion resistance of extrusion-clad, cast thorium alloys. Because considerable work was required in preparation of the clad thorium alloys, only those alloys which showed some promise in the first phase were chosen to be clad with the Zircaloy-2.

II. ARC-MELTED THORIUM ALLOYS

Only those alloy additions which had some chance of success in improving thorium's corrosion resistance were investigated. The alloys chosen for study were based on (1) corrosion work at lower temperatures reported in the literature, (2) study of phase diagrams for solid solubility or possible unusual, corrosion-resistant phase, and (3) nuclear considerations.

A. Preparation of Alloys

The same base material was used for all these alloy additions, to eliminate variation of metallic impurities in the thorium as a possible cause for variations in corrosion properties. The alloy additions themselves were all of high purity (99% or better).

The charge, of thorium and alloy addition, was arc melted in a purified inert atmosphere within a unit[4] that produced a thorium alloy button weighing about 50 grams. Each alloy was melted a total of four times, the button being reversed between melts to ensure homogeneity.

B. Sample Preparation

The arc-melted buttons were then cold rolled to a reduction of approximately 25% in thickness or, in some cases, until edge cracking was noted. The purpose of this cold work was to break up the cast structure of the arc-melted button. The rolled surfaces were milled to remove surface contamination, and the samples corrosion tested either as-rolled or in a heat-treated condition. Just prior to corrosion test, the samples were polished through 2/0 metallographic paper and thoroughly cleaned.

C. Test Procedure

After initial weights and dimensions were taken, the samples were placed on stainless steel trays with Grade "A" distilled water in the autoclave. No attempt was made to insulate samples electrically from each other or from the body of the autoclave. When the autoclave reached about 230°F, a valve was opened slightly and steam allowed to blow off in order to eliminate dissolved gases in the water and to purge the dead air space in the autoclave. It took approximately two hours for the autoclave to reach 500°F, and it was maintained at this temperature $\pm$ 5°F for one hour. At the end of this time, the autoclave was removed from the heater and cooled quickly by quenching in a spray of water. After removal from the autoclave, the samples were dried with a soft, lint-free cloth; at the same time, the loosely adherent corrosion product was removed by gentle rubbing. After weighing, the sample was returned for another one-hour exposure. Samples were autoclaved in this manner a total of ten times. In some cases of severe corrosion this long test was impossible. The cumulative weight loss over the total time at temperature is reported in $mg/cm^2/hr$ as the average corrosion rate. Since corrosion causes a weight loss, there is a tendency for the surface area of the sample to decrease as the length of exposure increases. In instances of severe corrosion, samples had to be withdrawn from test for this reason. In all cases, the initial surface area was used in calculations. In addition, no account was taken of the corrosion occurring during the period of heating to temperature. Since these errors are opposing, some compensation undoubtedly occurs.

D. Corrosion Results

1. Thorium-Zirconium*

Zirconium appeared to be one of the most promising alloy additions to thorium. All reports in the literature on tests at lower water temperatures indicated that increasing zirconium content resulted in increasing corrosion resistance. Furthermore, zirconium is one of the

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* Unless otherwise noted, all alloy compositions in this report will be expressed in weight percent. ($^w/_o$).

few metals which shows any appreciable solid solubility in thorium[2] and there are no intermetallic compounds.

A series of arc-melted thorium alloys was prepared with varying zirconium content. After cold rolling, the samples were annealed at 1382°F (750°C) for one hour. The corrosion date are plotted in Fig. 1, where all the rates appear to be linear. The values for the corrosion rates are high compared to "bare end" corrosion data described later in the report. This may possibly be due to different metallurgical histories.

It will be noted in Fig. 1 that the thorium-zirconium alloy curves do not pass through the origin, unlike those for unalloyed thorium. The explanation for this is probably the fact that, as a convenience, the corrosion data were obtained as weight losses (of the loosely adhering corrosion product) rather than as absolute values of the total metal consumed. From the appearance of all samples after the corrosion product was wiped off, it was evident that some oxide remained. For each alloy, the thickness or amount of tightly adherent oxide was presumed to remain fairly constant after each exposure. The amount of tightly adherent oxide remaining on the surface of the corroded unalloyed thorium was negligible, in view of the high corrosion rate, so that the curve appeared to pass through the origin. Even the thorium-zirconium alloys corroded in 500°F water show corrosion rates sufficiently high so that the error in assuming the curves to pass through the origin is relatively small and decreases further with increasing exposure time. In reporting the corrosion data, it will henceforth be assumed that a plot of the weight loss versus time will go through the origin; thus the accumulated weight loss divided by the total number of exposure hour is taken as the average corrosion rate.

2. Thorium-Uranium and Thorium-Uranium-Zirconium

Uranium is soluble in thorium only to the extent of 0.7% or less at room temperature.[2] There are no intermetallic compounds in the thorium-uranium system. Although it was not anticipated that additions of uranium would result in improved corrosion resistance, it was hoped that the presence of uranium might be helpful in clad alloys. Furthermore, thorium-uranium alloys are of interest for reactor fuels.

A series of arc-melted thorium alloys was prepared containing additions of 5, 9, and 15% uranium, and a similar series of alloys containing, in addition, 2% zirconium. All these alloys were cold rolled without difficulty to a 25% reduction in thickness. Samples were heat treated at 1382°F (750°C) for one hour, then corrosion tested in 500°F water, with the results shown in Table I. Previous results on unalloyed thorium and Th - 2.2% Zr have been included for purposes of comparison.

It appears that at least up to 9% uranium in thorium and in Th - 2% Zr can be tolerated without a significant decrease in corrosion resistance. The reason for the rapid failure of the Th - 9% U - 2% Zr arc-melted alloy is not known. It can only be assumed that there was gross segregation in the alloy, since an extrusion-clad alloy of approximately the same composition showed bare end corrosion rates of about 100 $mg/cm^2/hr$.

3. Thorium-Silicon

There are indications in the literature that additions of silicon to thorium result in improved corrosion resistance at lower water temperatures. Two intermetallic compounds, Th_3Si_2 and $ThSi_2$, have been reported[2] in the thorium-silicon system. The compound Th_3Si_2 corresponds to 7.5 $^w/o$ Si. A series of arc-melted alloys was prepared containing up to 4% silicon, but all the alloys obtained were brittle. In cold rolling, the 2.5 and 4% silicon compositions cracked in the initial light pass, the 1.3% alloy showed edge cracking after 8.5% reduction, and the 0.5% alloy, after 11.5% reduction. All of the alloys were annealed at 1382°F (750°C) for one hour. The results of corrosion testing in 500°F water are shown in Table II.

The data indicates that increasing additions of silicon are beneficial. It might be assumed that the increase in corrosion resistance is due to the increased amount of intermetallic compound.

4. Thorium-Titanium

There are no intermetallic compounds in the thorium-titanium system and the solid solubility of titanium in thorium is less than 0.1%. A series of alloys containing 1, 2.5, and 5% titanium was arc melted and

cold rolled without difficulty to a 25% reduction in thickness. Samples from each alloy were obtained in the as-rolled condition and after heat treatments at 1472°F (800°C) and 1562°F (850°C) for six hours followed by air-cooling. The results of corrosion testing in 500°F water are shown in Table III.

It is obvious that there is a major effect of heat treatment. It seems unlikely, however, that this effect is due to the presence of titanium in the alloy, since, as pointed out previously, there is negligible solid solubility and no intermetallic compounds. It is more logical to assume that the differences observed would have occurred even without the presence of titanium. This effect will be further discussed when extruded alloys are compared to arc-melted alloys.

In regard to the effects of titanium alloying, titanium additions result in improved corrosion resistance. Direct comparison of the relative effectiveness of titanium additions, as compared to zirconium additions, in arc-melted alloys was not possible because of the different heat treatments given the two sets of alloys. It is, however, the opinion of the writer that titanium additions are less beneficial than zirconium additions to corrosion resistance.

5. Miscellaneous Alloys

The last series of arc melts was a group of miscellaneous alloys which for a variety of reasons were deemed worthy of investigation. These alloys included 1% additions of nickel, iron, and copper, and a 0.5% addition of manganese. All the alloys were cold rolled and heat treated at 1472 and 1562°F. Samples from each were corrosion tested in 500°F water in the as-rolled and in the heat-treated conditions. In most cases corrosion rates could not be determined because of disintegration of the samples.

III. CLAD THORIUM ALLOYS

The use of thorium or a thorium alloy as the fuel in a water-cooled reactor presumes that the metal will be clad for protection against corrosion; theoretically then, the only concern is the corrosion resistance of

the cladding. Realistically, however, consideration must always be given to the possibility that one of the many fuel elements that go into a reactor will have a defective cladding. In terms of safety and production, a catastrophic failure could be very costly. The ideal fuel element should not show progressive corrosion of the core alloy when it is accidentally exposed through defects in the cladding. A compromise would be a fuel element which, when defective, would corrode slowly enough for failure detection and element removal before the danger point was reached.

The corrosion resistance of a number of thorium alloys extrusion-clad with Zircaloy-2 has been investigated. Two types of tests were made on samples of the extruded rods. In the first test, the corrosion rates were determined in high temperature water by exposing the clad samples with the core alloy exposed at the ends. In the second test, Zircaloy-2 plugs were welded on the ends of the samples, and the core alloy exposed to the high temperature water by means of a small (0.007-inch diameter) artificial-defect hole drilled through the cladding. The effects of water temperature and heat treatments on corrosion resistance were determined, and the bond strengths between the Zircaloy-2 clad and the thorium alloy cores were measured.

A. Preparation of Extrusion-clad Thorium Alloys

1. Casting

The first step in the production of clad thorium alloys was the preparation of the alloy. Thorium metal and the alloy addition were charged into a graphite crucible coated with MgOZrO to minimize carbon pickup. This alloy was then induction vacuum melted and bottom-poured. The resulting ingots were 2 inches in diameter and about 10 inches long.

2. Analyses

The ingot was analyzed top and bottom for alloy content and homogeneity, and the carbon content checked to ensure that excessive amounts of carbon had not been introduced. The intended compositions and actual analyses are shown in Table IV.

In most of the alloys the top and bottom analyses were reasonably close, indicating good homogeneity. All billets for extrusion were cut from the bottom of the casting so that the actual alloy content of the extruded rods was probably closer to the bottom analyses. Henceforth, the alloys will be identified by actual bottom analyses.

The variation of the carbon contents and the pickup in these alloys did not appear to be excessive. Work by S. Isserow[1] on the effect of carbon on hot water corrosion of thorium showed that increasing amounts were, in fact, beneficial, although the amounts needed to show significant improvement were far in excess of the amounts found in the present alloys.

3. Extrusion

The billets were cut from the bottom of the cast thorium alloy ingots, and machined on all faces to the proper dimensions. The billet with a Zircaloy-2 sleeve was canned and extruded. Details of the assembly are shown in Fig. 2.

All components were thoroughly cleaned before assembly. The copper internal cut-off, which also served as the cap, was welded to the copper can containing the copper nose plug, Zircaloy-2 sleeve, and the thorium core material. After leak testing, the can was evacuated to less than 0.04 micron and sealed at the copper evacuation tube. The sealed can was heated to temperature and extruded in a 2-inch liner through a 0.350-inch die for a reduction ratio of approximately 33:1. The liner, die and steel nose cone were all at a temperature of 900°F. In Table V, the extrusion force and temperature are listed for all the alloys.

The copper can was removed by pickling in nitric acid. After the end defects were cut off, the remaining Zircaloy-2 clad thorium-alloy rod was about 50 inches long. The clad thickness averaged 0.027-0.028 inch. The rod was then sectioned for various tests. In the results of these tests, there were no apparent differences that could be attributed to the samples' position in the extruded rod.

B. Sample Preparation

The two means by which the corrosion resistance of a clad thorium alloy was evaluated were the bare-end and the defect corrosion tests.

1. Bare End Corrosion

Samples for this test were about 1 inch long. Each end, having a cross section of its thorium alloy core exposed, was hand-polished through 2/0 metallographic paper; when samples were heat treated, their final polishing was done afterwards. The area used to calculate the weight loss was that of the exposed thorium alloy core on both ends.

2. Defect Corrosion Test

Defect corrosion specimens were cut to be 2 inches long, and the core alloy machined out of each end for a depth of about 1/4 inch. A plug of Zircaloy-2 was made to fit each end, and heliarc welded to the clad so that the thorium alloy was completely protected along the length and ends by Zircaloy-2. To ascertain the integrity of the welds, samples were exposed to 650°F water for a period of at least three hours. Failures due to poor welds were frequent so that many duplicate samples were required. On the other hand, the welds surviving this pre-test exposure could be expected to survive in defect corrosion test in 500°F water.

The corrosion-tested, welded samples were defected in the middle by drilling a 0.007-inch hole through the clad and extending 0.002 inch into the core. The required depth of the hole was obtained from a measure of the clad thickness of the sample on the ends before machining for the end plugs. A gage attachment to the drill press gave the depth of the hole drilled. An actual measure of the depth of the hole was made by focussing a metallographic microscope successively on the top and bottom of the hole. After they had been provided with such defects, the samples were heat treated and corrosion tested without further processing except for degreasing and cleaning.

C. Test Procedure

Corrosion testing procedure on bare-end or defect samples was similar to that for the arc-melted alloys.

The bare-end samples were exposed for one-hour intervals; the weight loss per unit area of thorium core alloy was calculated after each exposure. The advantage of the bare-end corrosion test over the unclad thorium alloy test was that the surface area remained constant during all exposures regardless of the corrosion rate.

Defect corrosion samples were run for longer intervals. The most pertinent information to be derived from this type of test was the exposure time required to cause failure or splitting of the clad.

D. Corrosion Results - Bare End

1. Effect of Temperature - The effect of temperature on the corrosion rates of some thorium alloys was investigated. All of the materials were tested in the as-extruded condition.* The corrosion rates, expressed as a weight loss in $mg/cm^2/hr$, in 400, 450 and 500°F water are shown in Table VI.

An Arrhenius plot of the data in Table VI was made, as shown in Fig. 3, where the log of the corrosion rate expressed as a weight loss in $mg/cm^2/hr$ was plotted against the reciprocal of the absolute temperature (°K). From the slope of the line the activation energy was calculated.

With the exception of the Th - 8.8% Zr and Th - 10.3% Zr alloys, all of the alloys corrosion tested at the three different temperatures gave a straight line in the Arrhenius plot; the activation energy could thus be calculated. It is believed that the exceptions were not due to any change in corrosion mechanism but rather to fixed errors in the data where the corrosion is measured as a weight loss rather than the total metal oxidized. After exposure, samples were rubbed gently with a cloth to remove corrosion product. It was obvious from their appearance that this technique did not

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* See Table V for extrusion temperatures.

remove all of the oxide. Where the corrosion rate was low during the 400°F water exposure of the Th - 8.8% Zr and Th - 10.4% Zr alloys, there was appreciable error because of incomplete removal of the corrosion product from the samples. Both of the alloys, in fact, showed weight gains after the first hour of exposure to 400°F water. Elimination of the first two hour exposures and recalculating the average weight losses over the remaining 8 hours resulted in higher corrosion rates for the alloys in 400°F water. The recalculated rate for the Th - 8.8% Zr alloy was 3.5 $mg/cm^2/hr$ as compared to the initial value of 3.1 and the recalculated rate for the Th - 10.4% Zr alloy was 3.0 $mg/cm^2/hr$ as compared to the initial value of 2.3. Using the recalculated rates in 400°F water for both alloys, straight lines were obtained in the Arrhenius plot in Fig. 3, and the calculated activation energies were now 14.9 Kcal/mol for the Th - 8.8% Zr and 16.4 Kcal/mol for the Th - 10.4% Zr alloy.

The value of the Th - 5.1% Zr was 14.9 Kcal/mol from Fig. 3. Within probable limitations of the data, all of the values for the 5.1, 8.8 and 10.4% Zr alloys were essentially the same. The Th - 2.8% Zr alloy showed a higher activation energy than even the unalloyed thorium (25.3 versus 21.4 Kcal/mol). It would appear that the beneficial effects of small additions of zirconium are overshadowed by the rapidly increased attack of thorium at higher temperatures.

From data in reference (3), the activation energy for the corrosion of uranium in water was calculated to be about 17 Kcal/mol. Unalloyed thorium showed an activation energy of about 21.4 Kcal/mol indicating that the corrosion rate of thorium increased more rapidly than that of uranium with increasing temperature. The ternary alloys of Th-U-Zr from Fig. 3 had activation energies of 16.7 and 18.8 Kcal/mol.

2. Effect of Heat Treatment - The clad thorium alloys were heat treated primarily in an attempt to improve the corrosion behavior of defected specimens by improving the bond between the cladding and the core. At the same time, the effect of heat treatment on bare-end corrosion in 500°F water was studied.

The effects of heat treating a Th - 2.8% Zr clad alloy at different temperatures are shown in Table VII. All of the heat treatments resulted in improved corrosion resistance compared to the as-extruded material. Increasing temperatures of heat treatment appeared to be beneficial, but it was noted that the higher temperatures impaired the bond between the core and clad. In a qualitative test, the 1562°F (850°C) heat treatment showed no apparent effect on the bond strength and, for this reason, subsequent heat treatments did not go beyond 1562°F. The sample quenched from 1562°F showed the lowest weight gain. This heat treatment reduced the corrosion rate by a factor of about two compared to the as-extruded sample.

The results of bare-end corrosion testing of clad thorium alloys with various heat treatments are shown in Table VIII. All samples were autoclaved for one-hour intervals in 500°F water up to a maximum of 10 hours. Many of the samples showed bulging and splitting of the clad at the ends before 10-hours exposure. The numbers in parentheses following the corrosion rates, expressed as weight loss in $mg/cm^2/hr$, are the total exposure times, in hours, before bulging and/or splitting of the clad at the ends occurred. The corrosion rates for these samples were averaged over the indicated intervals.

The Th - 2.8% Zr was the only one of the thorium-zirconium binaries which showed any major effect of heat treatment. The other thorium-zirconium binaries showed relatively little. There was some indication that the as-extruded samples had slightly better corrosion resistance. In addition, swaged samples of the 5.1 and 8.8% Zr alloys showed slightly improved corrosion resistance compared to the as-extruded samples. Increase of the zirconium content from 2.8 to 5.1% resulted in a radical improvement in the corrosion resistance, but further increase resulted in no apparent benefits. In fact, all of the zirconium alloys after 2.8% Zr showed essentially the same corrosion rates.

All of the Th - 5.1% Zr samples marked with an asterisk (*) in Table VIII behaved peculiarly in that the average corrosion rate decreased with increasing exposure time. The rod corrosion samples were sectioned

longitudinally and their cores lifted away from the clad. Since corrosion product was evident throughout the interface, it was apparent that the ten-hour exposure of the bare-end samples of the Th - 5.1% Zr alloys had resulted in the attack penetrating along the interface for the entire length of the sample. The weight losses from the ends were partially canceled by this penetration attack where the corrosion product was retained. The net effect was a decrease of apparent weight loss with increasing exposure. It was for this reason that the values of the initial rates were used for the Th - 5.1% Zr alloy after one or two hours exposure. These initial rate values appear to fit the other data more reasonably. After ten hours exposure the apparent average rates of corrosion had decreased by a factor of two over the initial rates. Corroded samples of other alloys were sectioned but in no other case was there any evidence of any appreciable penetration of the interface attack.

The corrosion rates of the thorium-uranium alloys were all very high, higher than for unalloyed thorium. Comparing the Th - 9.6% U with the Th - 9.9% U - 2.3% Zr, the presence of the zirconium in the ternary alloy decreased the weight loss by a factor of roughly 2-1/2.

The corrosion data on Th-U-Zr alloys in Table VIII appear to indicate that the as-extruded samples nave somewhat better corrosion resistance than the heat-treated samples. The samples annealed and water quenched from 1562^{o}F show approximately the same corrosion rates as the as-extruded samples. However, it was noted that the annealed and quenched samples bulged at the ends a good deal sooner so that there is a possibility of deterioration of the corrosion resistance of the interface as a result of the heat treatment. Comparing the binary Th - 2.8% Zr alloy with the ternary Th - 9.9% U - 2.3% Zr alloy, the corrosion rates are very roughly about the same except for the annealed and water-quenched sample of the Th - 2.8% Zr alloy. Thus, under certain conditions the presence of about 10% of uranium in thorium-zirconium appears to have relatively little effect on corrosion. However, upon increasing the amount of uranium to 13.1%, the increase in corrosion rate accelerates disproportionately from what would be expected due to the relatively slight increase in uranium content.

3. Comparison with Corrosion of Arc-melted Alloys - Comparison of the corrosion data in 500°F water of arc-melted thorium alloys in Table I with the data from bare-end corrosion tests of clad thorium alloys, Table VIII, showed uncertain correlation. There was a large discrepancy in the corrosion rates of unalloyed thorium. The arc-melted material showed a weight loss of 317 mg/cm^2/hr whereas the as-extruded, extrusion-clad thorium gave a rate of 150 mg/cm^2/hr. It is more than likely that this variation was due to the different fabrication histories. S. Isserow[1] reported corrosion rates for extrusion-clad thorium of 110 to 700 mg/cm^2/hr depending on the heat treatment.

When corrosion data on arc-melted thorium-zirconium alloys from Fig. 1 are compared with the results of clad extruded alloys in Table VIII some discrepancy is evident. The arc-melted Th - 2.2% Zr shows a weight loss of 102 mg/cm^2/hr, which compares favorably with a rate of 121 mg/cm^2/hr for the extruded Th - 2.8% Zr alloy. However, the arc-melted alloys containing 6.1 and 6.9% Zr show rates of 80 and 59 mg/cm^2/hr while extruded alloys containing 5.1, 8.8 and 10.4% Zr all show corrosion rates of 25 mg/cm^2/hr in 500°F water. These differences have not been explained.

4. Discrepancy in Corrosion Rates Due to Heating to and Cooling from 500°F - All of the corrosion test data were based on accumulated test periods of one to ten hours. The calculation of corrosion rates allowed only for the time at the test temperature and did not take into account the time of heating and cooling, when significant corrosion must occur. Approximately two hours were required for the autoclave to reach the test temperature 500°F. After one hour at temperature, the autoclave was removed from the heater and cooled rapidly, by quenching in a spray of water. To determine the amount of corrosion attributable to heating to and cooling from 500°F, samples were heated to 500°F in an autoclave. After reaching temperature the autoclave was quickly cooled in the manner standard for all test runs. The weight loss occurring during this time, compared to the corrosion rate ordinarily reported, is shown in Table IX.

It is apparent that the corrosion which occurs in the heating and cooling intervals represents a significant portion of the total corrosion for a one-hour test exposure. Based on the limited data in Table IX, it

would seem that 10-30% of the total corrosion of nominal one-hour test can be attributed to the heating and cooling interval. Thus, it may possibly be assumed that the absolute corrosion rates reported in this investigation are 10-30% on the high side.

E. Corrosion Results - Defected Clad

It has been mentioned previously that one of the primary goals of this investigation was the development of a thorium alloy which would be capable of surviving, without catastrophic failure, exposure to high temperature water through small defects in the cladding. For evaluation purposes, it was necessary to introduce an artificial defect, that is, a 0.007-inch hole drilled through the Zircaloy-2 cladding and extending 0.002 inch into the core alloy.

The ability of a particular alloy to survive catastrophic failure during defect corrosion testing is probably related to the following properties:

1. Corrosion resistance of the core alloy.
2. Bond strength between the Zircaloy-2 cladding and the thorium alloy core.
3. Ability of the corrosion product of the core alloy to pack in the defect and thus limit the access of water to the core alloy for further attack.
4. Strength of the core alloy in preventing cracking during corrosion.

The thickness of the cladding would undoubtedly influence the corrosion life of defected samples, but in this investigation cladding thickness was held reasonably constant at 0.027-0.028 inch.

Alloying of the thorium was viewed as a means of strengthening the bond as well as improving the corrosion resistance. Heat treatment of the coextruded rod was performed as an attempt to achieve stronger bonds

by the formation of a diffusion band (see Fig. 4). Alloy additions of uranium were made hoping that the packing of the corrosion product in the defect would be aided, thereby limiting the access of water for further attack. Uranium additions would have the further effect of strengthening the core alloy.

The results of defect corrosion testing in 500°F water of thorium alloys extrusion-clad with Zircaloy-2 are shown in Table X.

Generally, failure of samples was initiated by the formation of a small bulge at the defect. This increased in size with continued exposure until finally the cladding cracked and split. Splitting of the cladding usually occurred some distance away from the defect in the samples that failed slowly. When the split was large enough to permit visual exposure of the core alloy, the failure was termed catastrophic.

Thorium (unalloyed) - The as-extruded samples failed catastrophically in less than 24 hours. Work by S. Isserow[1] showed that various diffusion anneal treatments still did not prevent catastrophic failure of similarly defected, extrusion-clad samples in less than 24 hours.

Th - 2.8% Zr - Heat treatment of this alloy extended the defect corrosion life. It will be recalled that heat treatment also resulted in improved corrosion resistance of the core. Figure 4(a) shows a photomicrograph of the as-extruded cladding-core interface. Figure 4(b) shows the same material after a diffusion anneal at 1562°F (850°C) for 8 hours followed by air-cooling. The diffusion zone, which was more or less typical for all alloys, was measured to be about 0.003 inch thick. Figure 5 is a macrophotograph of a defected sample exposed to 500°F for 59-1/2 hours and then sectioned transversely through the 0.007-inch defect. Splitting of the clad can be seen on both sides of the defect. It will also be noted that the attacked area shows a network of cracks. Additional samples of this alloy were tested (not listed in Table X) after higher annealing temperatures. A defected sample annealed at 1742°F (950°C) for 8 hours failed catastrophically in 500°F after only 9 hours exposure. Samples annealed at 1652°F (900°C) for 4 and for 24 hours failed after 65-1/2 and

59-1/2 hours, respectively. The higher temperature (1742°F) was definitely detrimental whereas 1652°F was no more effective than the lower temperatures shown in Table X.

Th - 3.1% Zr - All samples showed relatively poor defect corrosion life. The cause of this was obvious after a corroded sample was sectioned (see Fig. 6). The attack appeared to have proceeded preferentially around the entire interface. This same effect had been noted in bare-end corrosion tests. The reason this particular alloy behaved in this fashion could not be determined.

Th - 8.8% Zr - The longest life (132 hours) was obtained on an as-extruded sample of this alloy. Another sample annealed at 1562°F and air-cooled had a defect corrosion life of 115 hours. However, the two other samples in this series lasted only about half the time so that any correlation on the effect of heat treatment was uncertain. A sectioned, corroded sample with a life of 115 hours (see Fig. 7) showed that over half the cross section of the core alloy beneath the defect had been attacked. Furthermore, the attack still appeared to progress preferentially along the interface.

Th - 10.4% Zr - From bare-end corrosion results it was expected that this and the preceding alloy would behave similarly. This hardly appears to be the case from the data in Table X. A corrosion life of 7-1/2 hours was obtained on one of the samples.

Th - 9.9% U - 2.3% Zr - This ternary alloy behaved favorably in comparison with the binary thorium-zirconium alloys. A sectioned, corroded sample (Fig. 8) indicated that in the case of the ternary alloy containing uranium, the area of attack underneath the defect appears more confined. The Th-U-Zr alloys showed higher corrosion rates in bare-end corrosion than the thorium-zirconium alloys. However, in defect tests it appears that the presence of uranium aids in packing of the corrosion product in the defect so that the attack was slowed down but not entirely stopped. The as-extruded sample and the sample annealed at 1562°F and water-quenched showed the longest lives.

Th - 13.1% U - 2.1% Zr - The defect corrosion life of samples of this alloy appear in general to be shorter than that of the Th - 9.9% U - 2.3% Zr alloy. This paralleled the results in bare-end corrosion tests where the ternary alloy with the higher uranium content showed decreased corrosion resistance.

Th - 9.6% U and Th - 15.6% U - All samples of both core alloys failed catastrophically in less than 17 hours. This could be due to poor corrosion resistance of the core alloy and/or poor bond.

Th - 1.3% Si - 1.8% Zr - The core alloy of this composition showed no promise in any of the corrosion tests.

Additional defect corrosion tests were run in 400°F water. The samples defected were in the as-extruded condition. The results are shown in Table XI. It was evident that lowering the temperature prolongs significantly the defect corrosion life but does not prevent eventual failure. The clad alloys which showed the longest time to failure in 500°F water follow the same trend in 400°F water.

Swaging of the Th - 5.1% Zr and Th - 8.8% Zr alloy before inserting the defect was attempted as a means of increasing corrosion life. No beneficial effects were noticeable in testing, either in 400 or 500°F water.

F. Bond Tests

There are indications that the bond strength between the extruded thorium core alloy and the Zircaloy-2 cladding plays a role in the ability of defected samples to survive exposure to high temperature water. A convenient method for qualitative testing was the notch-fracture test. A rod section about 1/2 inch long was cut longitudinally until the remaining thickness of the core was approximately equal to the cladding thickness. The partially cut halves were then pried apart. Good bonds caused a continuous break through the core and cladding whereas poorly bonded samples showed peeling or separation between the core and cladding during bending.

All of the samples, heat treated or otherwise, of the Th - 9.9% U, Th - 13.6% U, and Th - 1.3% Si - 2.1% Zr core alloys showed undeniably poor bonds by this method. Defect corrosion tests of these samples in 500°F water resulted in catastrophic failure in less than 17 hours. Notch-fracture tests on thorium-zirconium alloys heat treated at 1742°F showed all bonds to be poor. Heat treatments at 1652°F showed bad or borderline results so that on this basis it was decided early in the investigation to limit heat treatments to below 1652°F.

In most of the other alloys, the bond test results were less clean-cut so that it was desirable to obtain a quantitative measure of the bond strength. Zircaloy-2 studs were welded to the cladding. Sawcuts through the clad were made around the stud so that the applied stress in a tensile test acted on a limited area. The actual area was measured after the break. The results of these stud bond tests of the various alloys subjected to different heat treatments are shown in Table XII. The letters in parenthesis following the tensile stress indicate whether the specimen broke in the weld (W), bond (B), or core (C), thus determining the weakest point.

The data were not conclusive in establishing a general effect of heat treatment on bond strength. Poor defect corrosion resistance was noted for all cases of poor bond strength (thorium-zirconium alloys). On the other hand, good bond strength does not necessarily imply good corrosion resistance.

IV. SUMMARY

Based on the present investigation and past work reported in the literature, zirconium appears to be the most promising addition to thorium for improving thorium's corrosion resistance in high temperature water. In the range of compositions studied, increasing zirconium additions beyond 5% and up to 10% resulted in no further increase in corrosion resistance. All of the alloys in this range showed approximately the same corrosion rate at 500°F, that is, a weight loss of 25 mg/cm^2/hr. The corrosion resistance, in this range of composition only, was fairly insensitive to heat treatments.

Silicon additions to thorium, up to 4%, also resulted in improved corrosion resistance, though at best the thorium-silicon alloys were no better than the thorium-zirconium alloys. The thorium-silicon alloys were very brittle, particularly the higher silicon compositions.

The bare-end corrosion rates of various extrusion-clad thorium alloys were obtained in 400, 450, and 500°F water. From an Arrhenius plot of the data, the activation energy was obtained for the various alloys and for unalloyed thorium. The activation energies for thorium-zirconium and Th-U-Zr alloys ranged from 14.9 to 18.8 Kcal/mol compared to 21.4 Kcal/mol for unalloyed thorium. A Th - 2.8% Zr alloy showed an activation energy of 25.3 Kcal/mol.

The ability of clad thorium to survive exposure of the core to 500°F water entering through an intentional defect in the cladding was significantly improved by alloying with zirconium. Exposure of unalloyed thorium for only a few hours resulted in catastrophic rupture of the Zircaloy-2 cladding whereas the best thorium-zirconium alloy tested survived 132 hours at which time the cladding had only started to split. In spite of attempts to improve the core-clad bonds by heat treating to form a diffusion zone, the attack in the clad thorium-zirconium core alloy seemed to penetrate preferentially along the clad-core interface. Although the presence of about 10% uranium in a Th - 2% Zr core alloy appeared to confine the attack, rupture of the clad eventually occurred because of the increased volume of corrosion product at base of the defect. There was some evidence that increasing the uranium content beyond 10% in the ternary Th-U-Zr system had an adverse effect on its ability to resist failure in defect corrosion tests. A clad thorium alloy containing about 9% uranium and 5-10% zirconium might result in improved ability to survive defect corrosion.

Although defected samples in 400°F water required longer times for failure, all but one of the alloys failed in 260 hours or less. One sample of the thorium-zirconium alloy, which survived the longest (132 hours) in 500°F water, still showed no change after 343 hours in 400°F water at which time the test had to be discontinued to terminate the work on

schedule. Sectioning of the sample showed that the attack was progressing and that failure eventually would have occurred.

The ability of a clad (Zircaloy-2) U - 2% Zr alloy, after proper heat treatment, to survive defect corrosion for extended periods of time could not be duplicated when thorium alloys were substituted as the core material. Apparently, unlike the U - 2 ^{w}/o Zr alloy, the corrosion products of the thorium alloys do not have the property of packing at the base of the defect, thereby limiting the access of water for further attack.

V. TABLES AND FIGURES

TABLE I

Corrosion of Arc-Melted Th, Th-Zr, Th-U and Th-U-Zr Alloys in 500°F Water

Nominal Additions, w/o	Weight Loss, $mg/cm^2/hr$	Exposure, hours	Remarks
Th (unalloyed)	320	3	Uniform attack
2.2 Zr	100	4	Uniform attack
5 U	330	3	Uniform attack
9 U	350	3	Uniform attack
15 U	690	2	Sample breaking up
5 U - 2 Zr	100	5	Uniform attack
9 U - 2 Zr		1	Disintegrated
Th - 15 U - 2 Zr	150	5	Uniform attack

TABLE II

Corrosion of Arc-Melted Th-Si Alloys in 500°F Water

Nominal w/o Silicon	Weight Loss, $mg/cm^2/hr$	Exposure, hours	Remarks
0.5	430	1	Partial disintegration - possible segregation
1.3	110	5	Uniform corrosion
2.5	140	5	Surface rough - uniform corrosion
4	63	5	Uniform corrosion

TABLE III

Corrosion Rates of Arc-Melted Th-Ti Alloys in 500°F Water

Weight Loss, $mg/cm^2/hr$

Nominal w/o Titanium	As-Rolled	Annealed at 1472°F 6 hrs.	Annealed at 1562°F 6 hrs.
1	82 (5)*	360 (3)	350 (3)
2.5	54 (5)	265 (3)	330 (3)
5	56 (4)	160 (3)	160 (3)

* Numbers in parentheses are total exposure times in hours.

TABLE IV

Analyses of As-Cast Thorium Alloys

Nominal Additions (W/o)	Composition, Weight Percent						C (ppm)
	Zr		U		Si		
	Top	Bottom	Top	Bottom	Top	Bottom	
2 Zr	*	2.81					575 400
5 Zr	5.12	5.12					1475 970
10 Zr	8.40	8.82					1075 940
15 Zr	9.63	10.37					515 450
9 U - 2 Zr	2.21	2.31	9.53	9.88			285 340
15 U - 2 Zr	2.07	2.07	15.08	13.11			450 440
9 U			9.37	9.57			495 710
15 U			14.75	15.63			870 810
1.3 Si - 2 Zr	1.46	1.77			1.27	1.29	285 340

* Original analyses for zirconium in this alloy showed good homogeneity, but the absolute values were found to be in error. The correct absolute value is shown for bottom.

TABLE V

Extrusion Temperatures and Forces - Thorium Alloys

Nominal Additions (w/o)	Extrusion Temperature (°F)	Extrusion Force (1) (tons)
2.8 Zr	1400	180
5.1 Zr	1400	235
8.8 Zr	1400	220
10.4 Zr	1400	170
9.9 U - 2.3 Zr	1525	170
13.1 U - 2.1 Zr	1450	150
9.6 U	1450	190
15.6 U	1450	250
1.3 Si - 1.8 Zr	1500 (2)	140

(1) Area reduction, 33:1.

(2) Initial attempt to extrude at 1400°F resulted in stalling of the press, which had a capacity of 300 tons.

TABLE VI

Effect of Water Temperature on the Corrosion Rate of Thorium Alloys

Nominal Additions (w/o)	Weight Loss, $mg/cm^2/hr$		
	400°F	450°F	500°F
Th (unalloyed)	14	52	150
2.8 Zr	6.9	7.3	120
5.1 Zr	5.1	12	25
8.8 Zr	3.1	11	24
10.4 Zr	2.3	9.6	26
9.9 U - 2.3 Zr	14	46	98
13.1 U - 2.1 Zr	22	72	165

TABLE VII

Effect of Heat Treatment on the Corrosion Rate of Th - 2.8 w/o Zr in 500°F Water

Heat Treatment				Weight Loss, $mg/cm^2/hr$	Exposure, hours
Temp		Time, hours	Cooling		
°F	°C				
1562	850	8	air	97	3
1652	900	8	air	89	2
1742	950	8	air	77	3
1562	850	6	water quench	65	5
As-extruded				120	2
Unalloyed thorium as-extruded				150	3

TABLE VIII

Corrosion Rates (Weight Loss, mg/cm^2/hr) of Thorium Alloys in 500°F Water

Additions (w/o)	Heat Treatment*					
	A	B	C	D	E	F
Unalloyed	150 (3)**					
2.8 Zr	120 (2)		94 (3)	65 (5)		
5.1 Zr	25 (2)	28 (2)	28 (2)	42 (1)	19 (1)	32
8.8 Zr	24	35	32	29	21	30
10.4 Zr	26	33	31	28		
9.9 U - 2.3 Zr	98	130 (8)	120	100 (3)		
13.1 U - 2.1 Zr	165 (8)	180 (3)	190 (6)	165 (1)		
9.6 U	260 (1)	310 (1)	550 (1)	450 (1)		
15.6 U	No rates possible. After 2 hours all samples bulged and split at ends.					
1.3 Si - 1.8 Zr	No rates possible. After 1 hour all samples bulged and split.					

* Key to Heat Treatments:
A - as extruded
B - 1472°F (800°C) anneal 6 hrs, air cool
C - 1562°F (850°C) anneal 6 hrs, air cool
D - 1562°F (850°C) anneal 6 hrs, water quench
E - swage
F - swage, anneal 1562°F (800°C) 6 hrs, water quench

** Numbers in parentheses are the total exposure times, in hours, before bulging and/or splitting of the clad at the ends occurred.

TABLE IX

Water Corrosion of Thorium Alloys in Heating and Cooling Intervals (500°F)

Alloy Additions (W/o)	Condition	Weight Loss (Heating and Cooling Interval) mg/cm^2	Corrosion Rate* Weight Loss, $mg/cm^2/hr$
8.8 Zr	as-extruded	5.0	24
8.8 Zr	as-swaged	2.0	21
10.4 Zr	as-extruded	8.7	26
9.9 U - 2.3 Zr	as-extruded	17.5	98

* Rate based on accumulated test periods of ten hours.

TABLE X

Results of Defect Corrosion Tests of Thorium Alloys in 500°F Water

Additions (W/o)	Heat Treatment*	Exposure, hrs. (Cladding Intact)	Exposure, hrs. (Cladding Failed)	Type of Failure
unalloyed	A		24	Catastrophic
2.8 Zr	A	--	24	Catastrophic
	B	42½	59½	Small splits
	C	24	40½	Slight split
	D	50½	67½	Catastrophic
5.1 Zr	A	17	34	Large splits
	B	5	20	Small splits
	C	5	25	Small splits
	D	18	36	Catastrophic
8.8 Zr	A	110	132	Very slight splits
	B	37	54	Catastrophic
	C	95	115	Split, very large bulge
	D	36	50½	Catastrophic
10.4 Zr	A	17	36	Small split
	B	51½	71½	Small split
	C	--	17	Welds appear to have failed
9.9 U	A	66	72	Small splits
2.3 Zr	B	19	36	Small splits
	C	36	42	Small splits
	D	67½	84½	Splits
13.1 U	A	36	53	Split
2.1 Zr	B	--	17	Split
	C	17	34	Catastrophic
9.6 U	A	--	17	Catastrophic
	B	--	17	Catastrophic
	C	--	17	Catastrophic
15.6 U	A	--	17	Catastrophic
	B	--	17	Catastrophic
	C	--	17	Catastrophic
1.3 Si	A	--	18	Catastrophic
1.8 Zr	B	--	?	Catastrophic
	C	--	?	Catastrophic
	D	--	?	Catastrophic

* Key to Heat Treatments: A - as-extruded
B - 1472°F (800°C) anneal 6 hrs, air cool
C - 1562°F (850°C) anneal 6 hrs, air cool
D - 1562°F (850°C) anneal 6 hrs, water quench

TABLE XI

Results of Defect Corrosion Tests of Thorium Alloys in 400°F Water

Additions (w/o)	Exposure, hrs. (Cladding Intact)	Exposure, hrs. (Cladding Failed)	Type of Failure
2.8 Zr	190½	260½	Catastrophic; entire core corroded away.
5.1 Zr	64½	86½	Very slight split* at some distance from defect.
8.8 Zr	342½**		
10.4 Zr	190½	260½	Very slight split* at defect.
9.9 U - 2.3 Zr	190½	260½	Split.
13.1 U - 2.1 Zr	86½	106½	Catastrophic.
9.6 U	20	42½	A number of very slight splits*
15.6 U	42½	64½	Small split.

* Noticeable only under magnification.

** No visible external change in defected sample. Sample was sectioned through defect and attack was evident at the bottom of defect. It was suspected that the attack would progress, leading to the eventual failure of the clad.

TABLE XII

Stud Bond Strength of Thorium Alloys Extrusion-Clad with Zircaloy-2

(Tensile Strength, psi X 10^{-3})

Additions ($^{w}/_{o}$)	As-Extruded	1472°F - 6 hrs. Air-Cooled	1562°F - 6 hrs. Air-Cooled	1562°F - 6 hrs. Water Quenched
2.8 Zr	25.5 (C)*	24.0 (C)	20.2 (C)	39.0 (B,C)
5.1 Zr	15.8 (B)	20.5 (B)	14.4 (B)	25.9 (B)
8.8 Zr	28.8 (C)	48.3 (C)	60.7 (C)	39.3 (C)
10.4 Zr	53.5 (C)	32.9 (C)	35.0 (C)	----
9.9 U - 2.3 Zr	30.9 (C)	33.1 (C)	29.2 (C)	27.9 (B)
13.1 U - 2.1 Zr	65.6 (W)	35.7 (C)	30.2 (C)	----
15.6 U	43.8 (W)	26.2 (C)	31.5 (B)	----

* Letters in parentheses refer to location of fracture, thus:

C - core

B - bond

W - weld

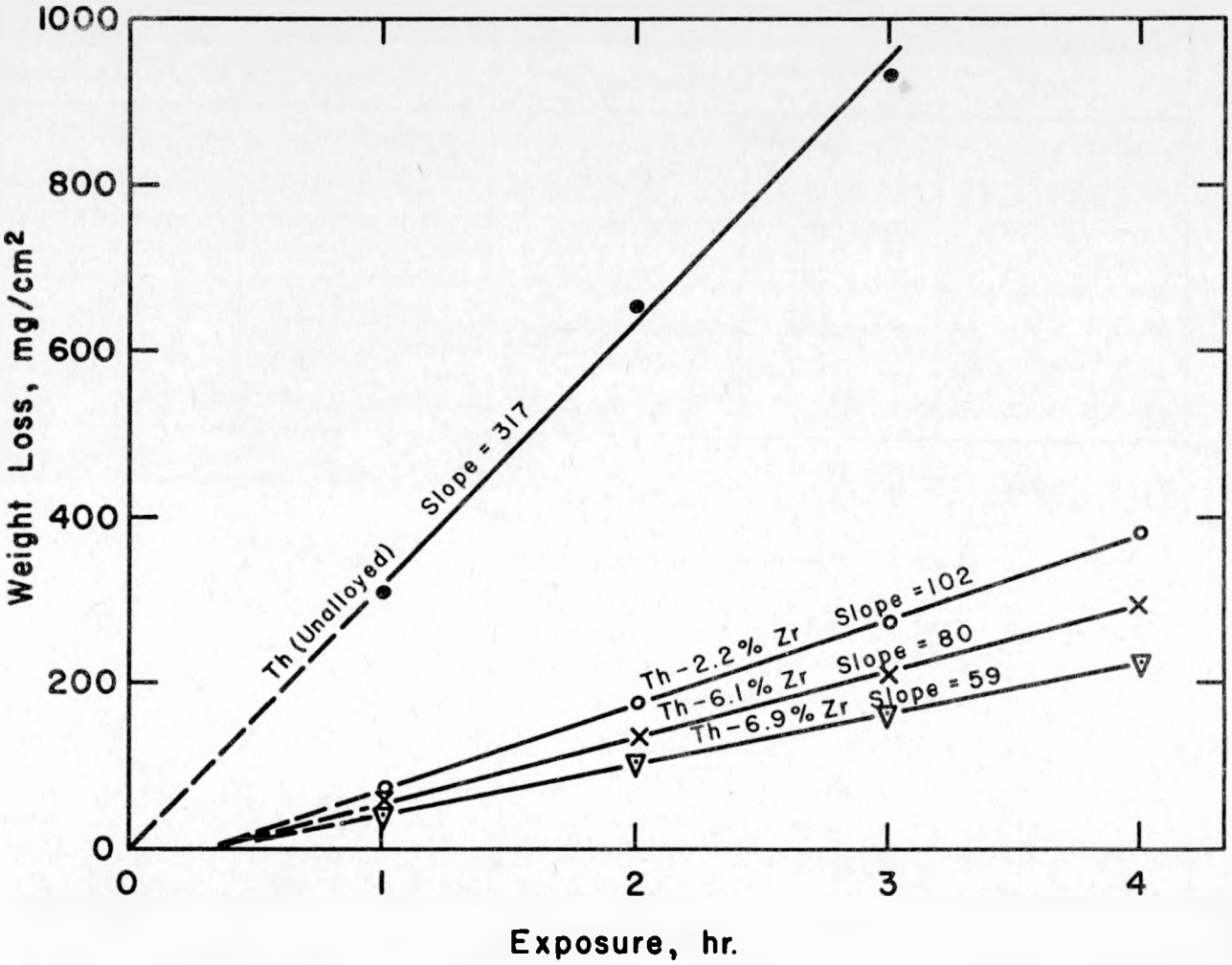


Fig. 1 - Corrosion of arc-melted thorium-zirconium alloys in 500°F water. Drawing No. RA-1093

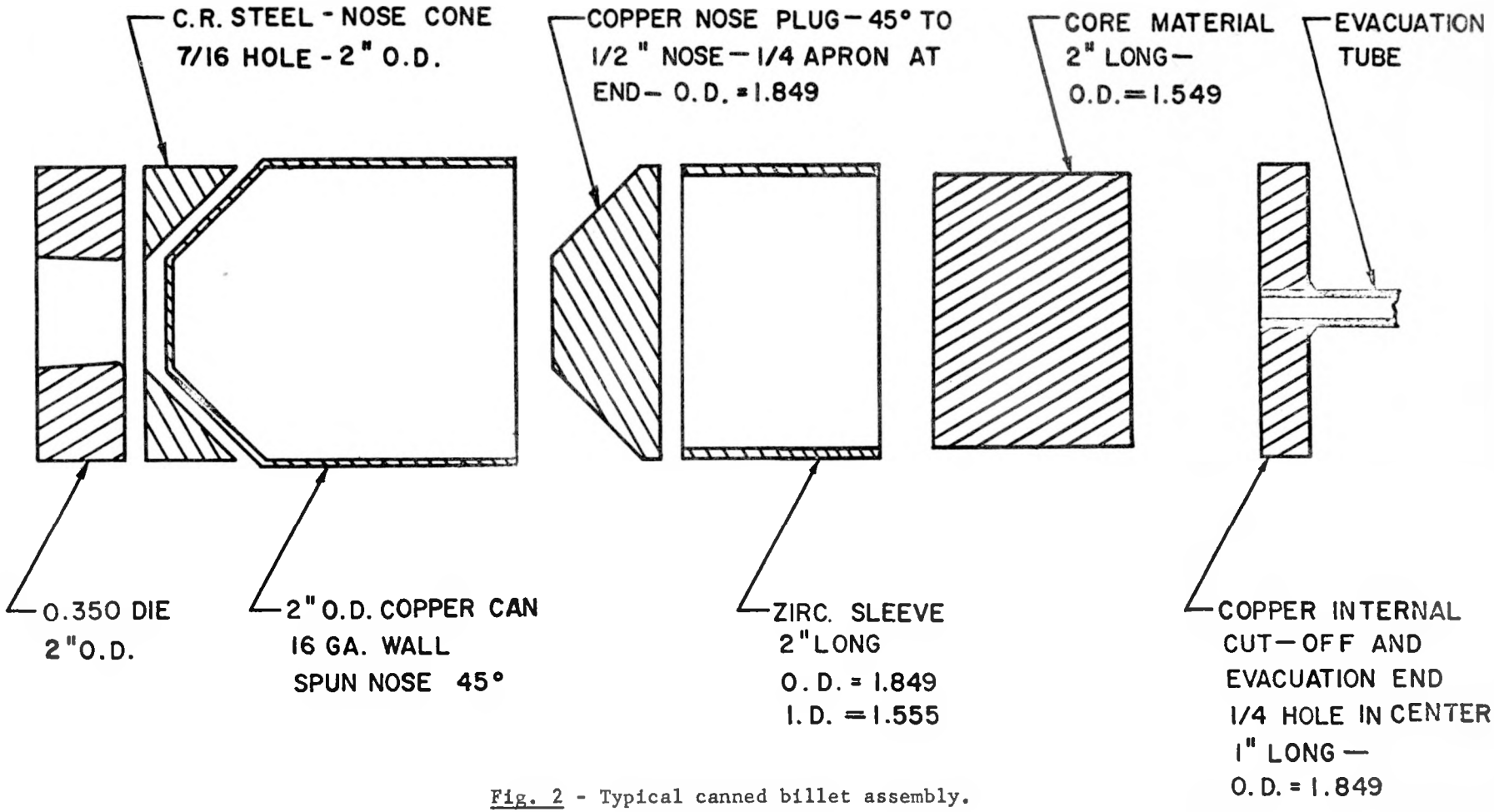


Fig. 2 - Typical canned billet assembly.

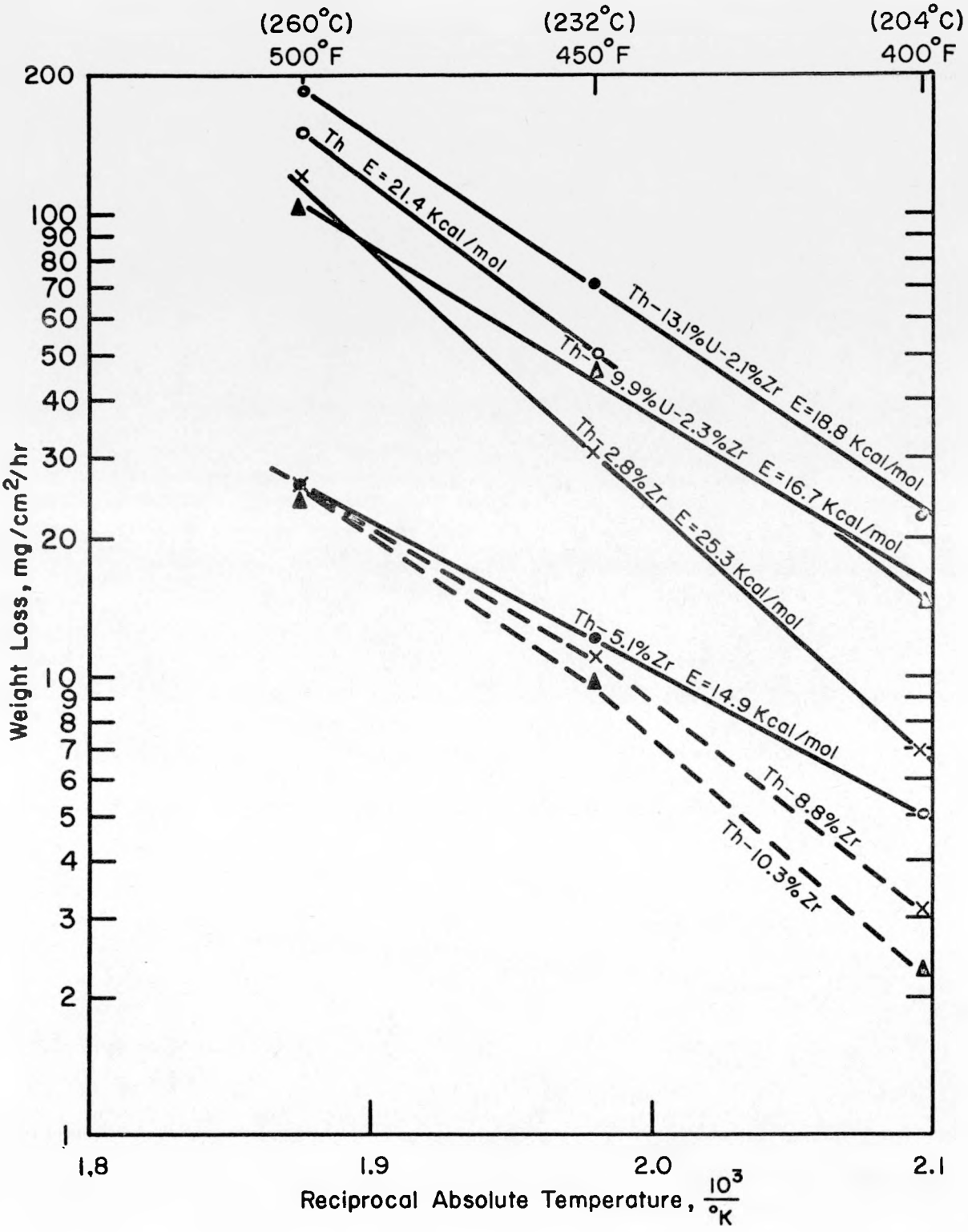
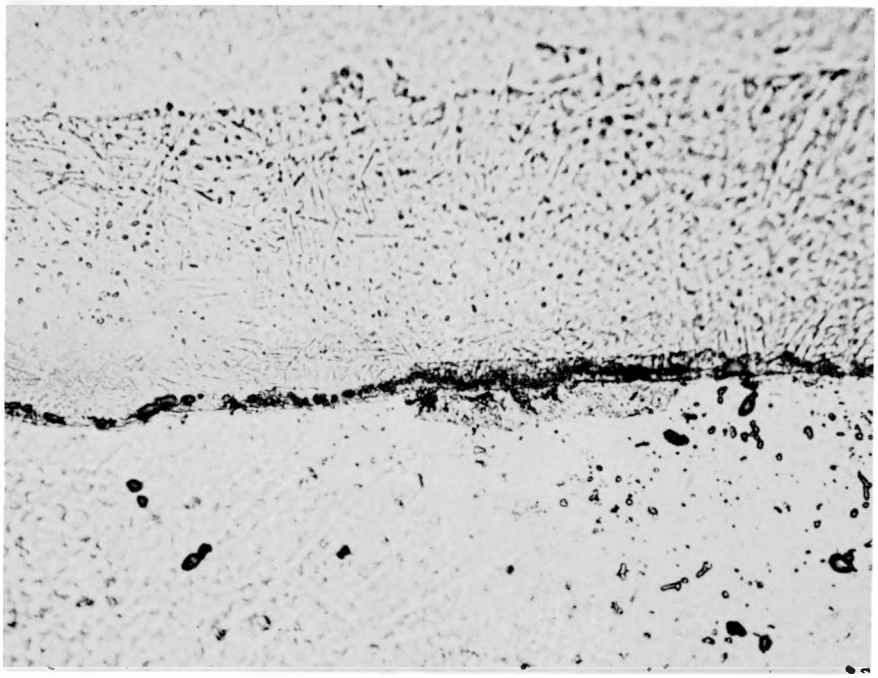


Fig. 3 - Temperature dependence of the corrosion rate of thorium alloys. Drawing No. RA-1065

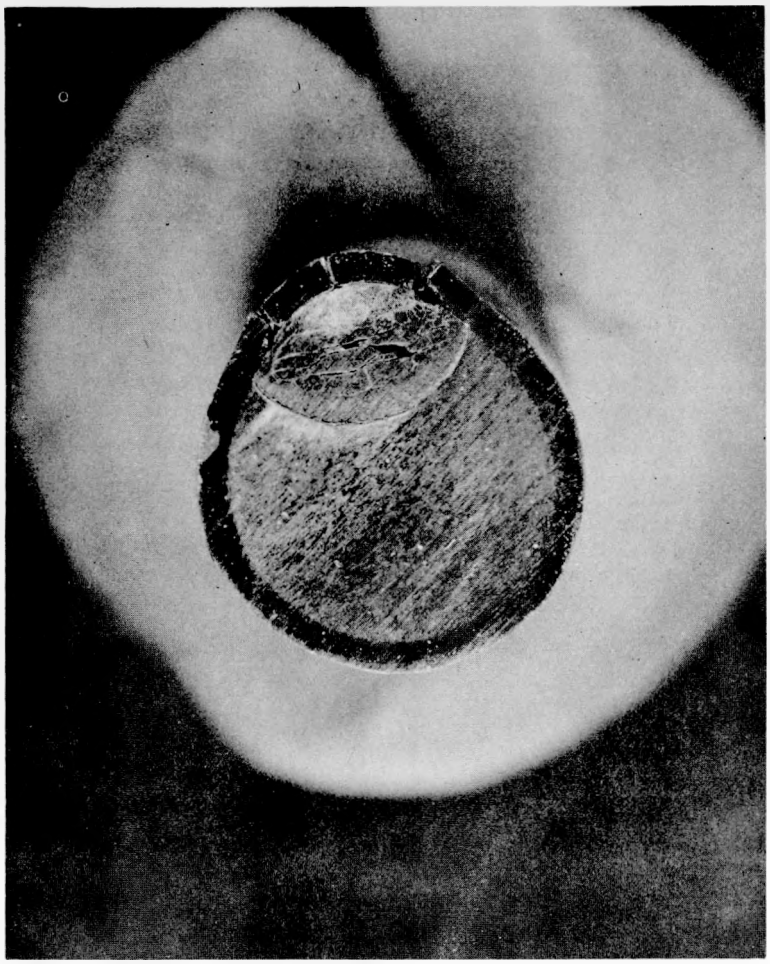
500X Bt. Lt. (a) as extruded A-2226-1



500X Bt. Lt. A-2226-2

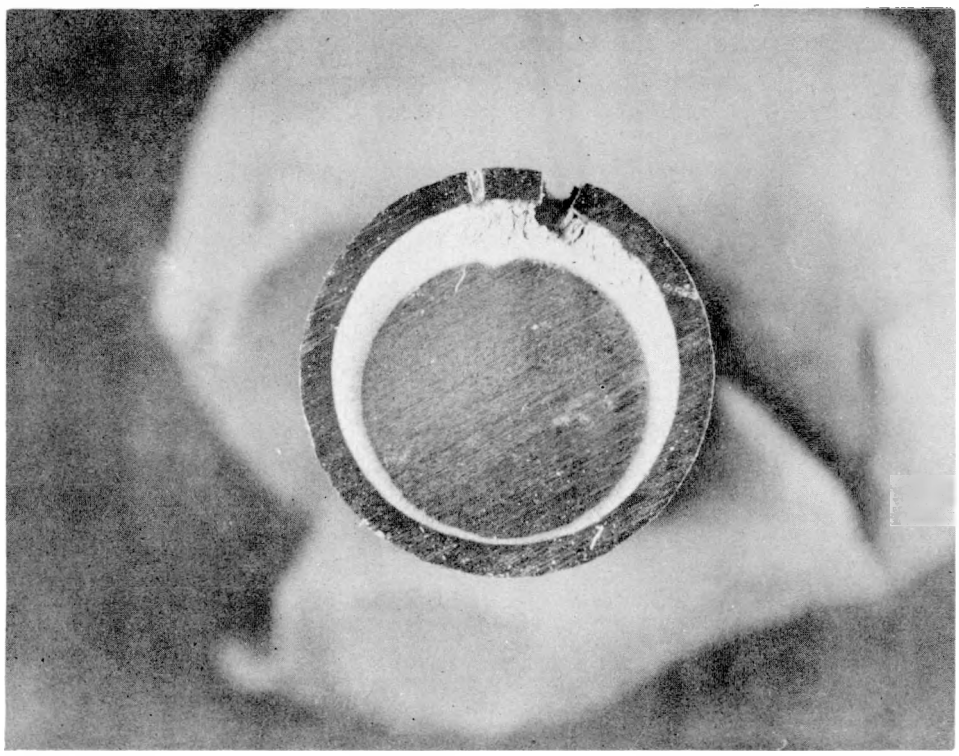
(b) 1562°F (850°C) anneal
8 hours, air-cool

Fig. 4 - Zircaloy-2 clad Th - 2.8% Zr. Zircaloy at top. Mechanical polish.



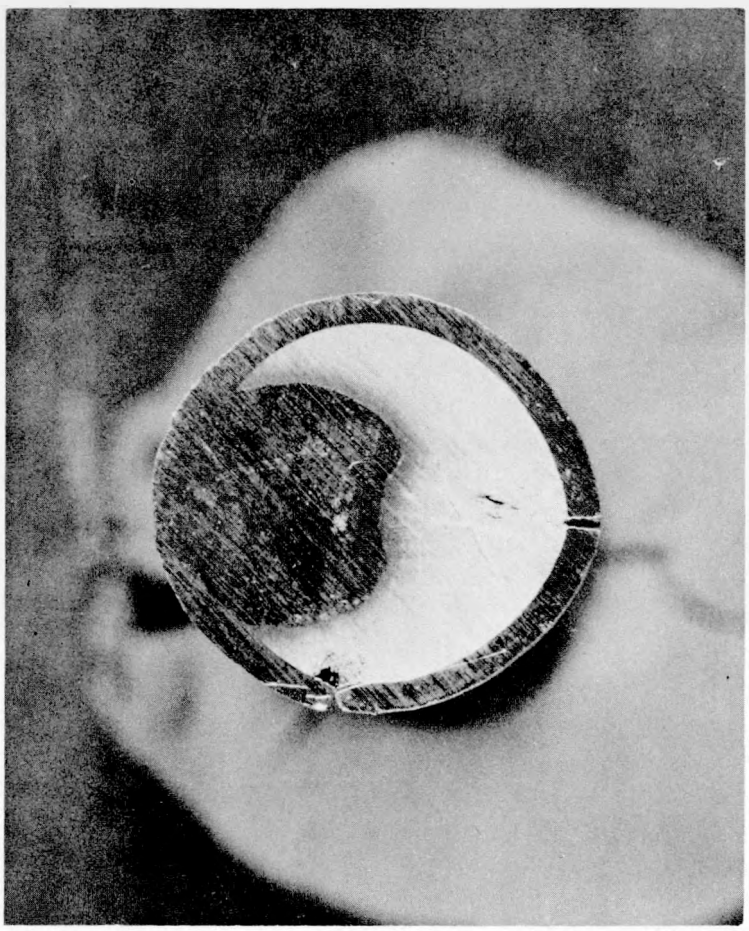
6X Bt. Lt. RF-6627-4

Fig. 5 - Defect corrosion specimen, core alloy Th - 2.8% Zr. Heat treated at 1472°F (800°C) for 15 hours, air-cooled. Exposure time to 500°F water was 59-1/2 hours. Transverse section through defect.



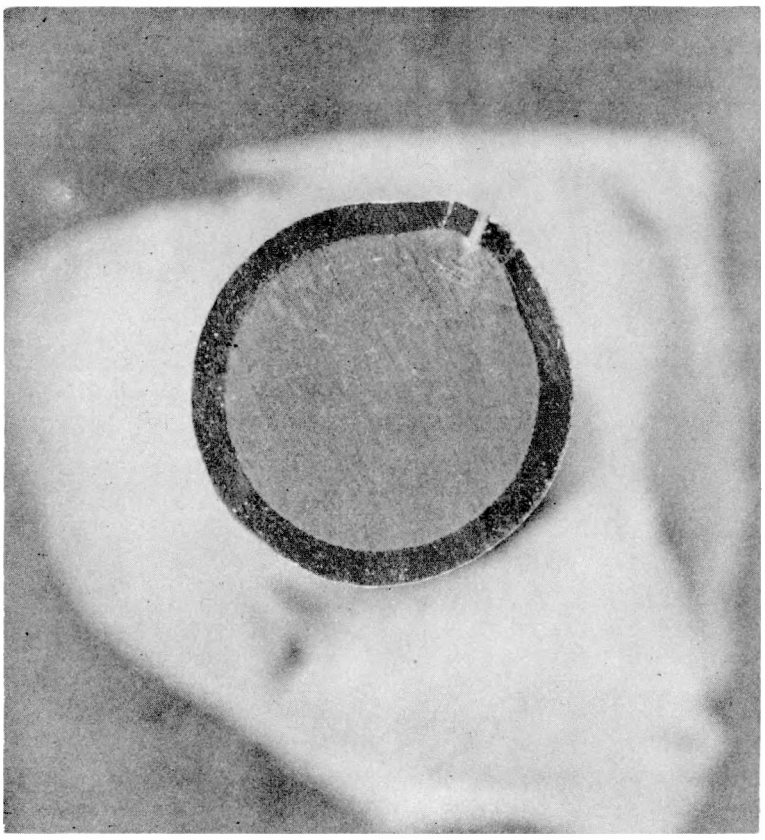
6X Bt. Lt. RF-6626-3

Fig. 6 - Defect corrosion specimen, core alloy Th - 5.1% Zr. Heat treated at 1562°F (850°C) for 6 hours, air-cooled. Exposure time to 500°F water was 25 hours. Transverse section through defect.



6X Bt. Lt. RF-6625-2

Fig. 7 - Defect corrosion specimen, core alloy Th - 8.8% Zr. Heat treated at 1562°F (850°C) for 6 hours, air-cooled. Exposure time to 500°F water was 115 hours. Transverse section through defect.



6X Bt. Lt. RF-6624-1

Fig. 8 - Defect corrosion specimen, core alloy Th - 9.9% U - 2.3% Zr. Heat treated at 1562°F (850°C) for 6 hours, air-cooled. Exposure time to 500°F water was 42 hours. Transverse section through defect.

VI. REFERENCES

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