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DIFFUSION ANNEALING AS A MEANS OF IMPROVING CORROSION RESISTANCE OF ZIRCALOY-2 CLAD, URANIUM–2 W/o ZIRCONIUM RODS

By
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April 11, 1960

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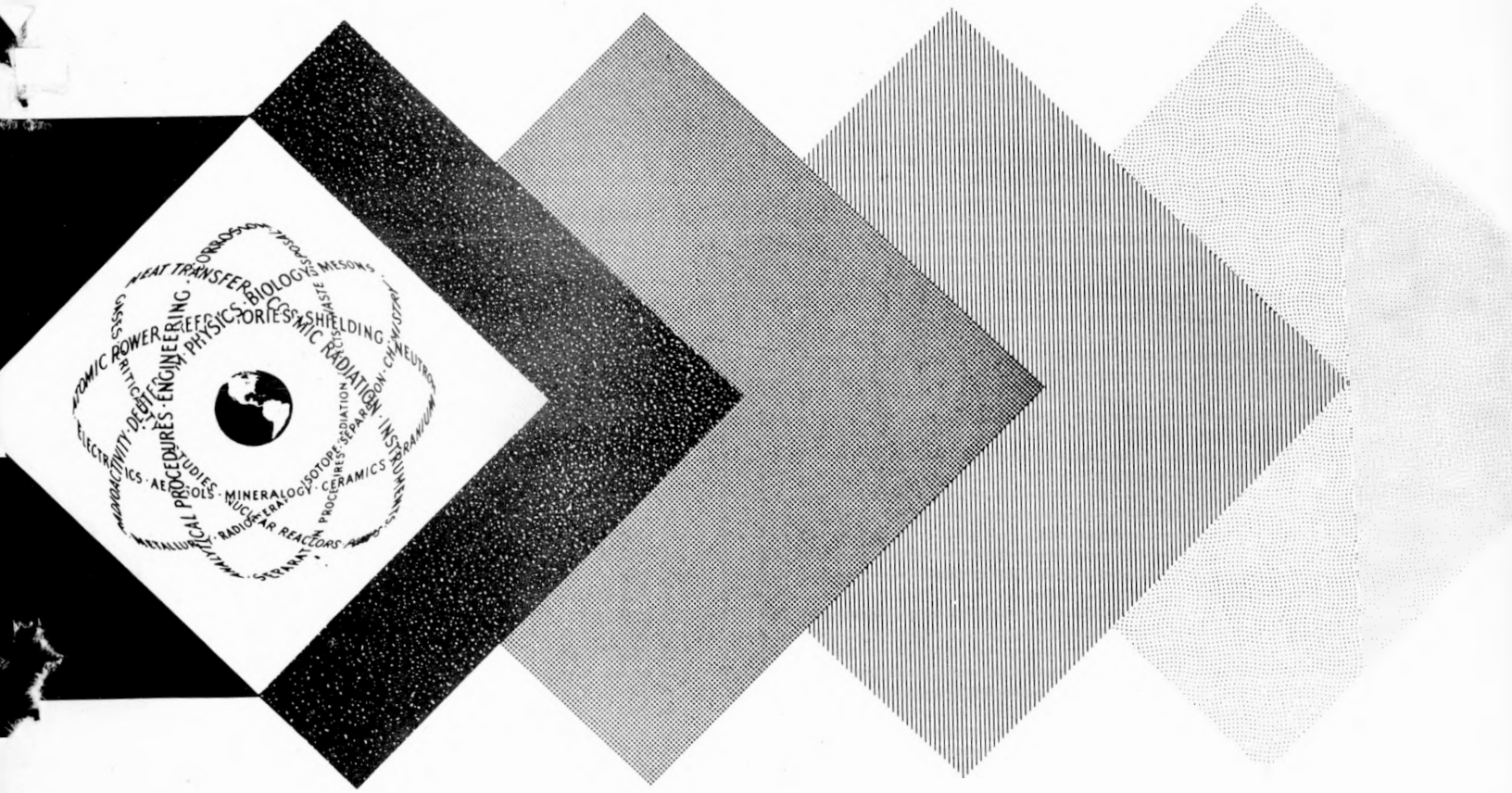
Concord, Massachusetts



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April 11,1960

Nuclear Metals, Inc.
Concord, Massachusetts

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Technical Director

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I. ABSTRACT AND SUMMARY

The diffusion heat treatment technique has been investigated as a means of improving the corrosion protection provided by Zircaloy cladding coextruded with rods of U - 2 ^{w}/o Zr alloy. Specimens with cladding defects in the form of drilled holes were tested in high temperature steam and water to determine the effects of various factors influencing the beneficial effect of the diffusion anneal. These included heat treatment time and temperature, cooling rates, secondary heat treatments, defect size, cladding thickness, hardness, bond strength, and radiation. Most of these factors appeared to affect the ultimate corrosion life of the defected specimens. In particular, all heat treatments from 800 to 1050^{o}C greatly increased the corrosion life if the time at temperature was sufficient; slow cooling rates or subsequent heat treatments between 650 and 700^{o}C were detrimental; a strong initial bond is desirable; the treatment does not reliably provide protection if the cladding is 10 mils thick or less. A few defected, irradiated specimens have survived subsequent short-time corrosion tests.

Tests were also performed on specimens with defects resulting from flaws placed in the cladding component prior to extrusion. Most of these specimens did not benefit from the diffusion anneal. The treatment was successful, however, in preventing the failure of specimens with threads of uranium extending between the core material and the exposed cladding surface.

The diffusion anneal technique continues to show promise as a means of increasing the reliability of the Zircaloy cladding on rods of U - 2 ^{w}/o Zr.

II. INTRODUCTION

Excellent corrosion resistance is required of nuclear fuel elements exposed to high temperature water or steam in various nuclear reactors. One way of utilizing desirable fuel alloys with low corrosion resistance is to clad them by coextrusion with Zircaloy. There is, however, a remote possibility that such cladding might contain minute holes which, by permitting direct attack of the core material by corrodant, would lead to rapid catastrophic failure of the fuel element.

Levine and Lamartin[1] worked with small, artificial cladding defects which caused immediate catastrophic failure of as-extruded, Zircaloy-clad U - 2 ^{w}/o Zr rods exposed to high temperature water or steam. They found that the failure of such rods began at the defect, where the forces exerted by the initial corrosion products caused the cladding to separate from the core, which then reacted with the corrodant in ever-increasing amounts as exposed.

By applying diffusion anneals to such artificially defected rods, core corrosion was limited to small pockets at the bases of the defects and catastrophic failure was prevented. Levine and Lamartin also determined the compositions of various layers of the diffusion zone at known distances from the original U - 2 ^{w}/o Zr - Zircaloy-2 interface.

Plots of these values (Fig. 1) showed that diffusion of zirconium into the core material adjacent to the cladding did not form a uranium-zirconium alloy of exceptionally high corrosion resistance. Instead, the relative rates of diffusion of uranium into Zircaloy, and vice versa, were such that the 50 ^{a}/o isoconcentration line moved from the cladding-core interface into the cladding.

These results, coupled with the observations of corrosion pockets at the bases of defects in diffusion treated rods, led Levine and Lamartin to discount the explanation which attributed the improvement in corrosion resistance simply to the formation of a highly corrosion resistant uranium-zirconium alloy in the outer layers of the core material.

Other explanations were proposed for the beneficial effect of the diffusion anneal technique. Microstructure studies showed a bending of

isoconcentration lines at the bases of defects in diffusion annealed specimens. Levine and Lamartin thought that this bending might indicate a partial "healing" of the defects. They estimated that the alloy formed at the defect bases contained 22 to 55 ^{a}/o Zr, and suggested that a thin protective layer rich in zirconium could have been formed by leaching the uranium from the material at the base of the defect during the early corrosion stages.

A hypothesis that the improved corrosion resistance resulted from removal of residual stress during the anneal was discounted when specimens failed corrosion tests after 1000°F stress-relieving anneals. A more plausible explanation is that the diffusion anneal improved the bond enough to prevent separation of the cladding which, in turn, confined the corrosion product so that it plugged the hole by self-compaction.

The program to be discussed below was concerned mainly with continuing corrosion tests of the original specimens prepared by Levine and Lamartin, and expanding their studies.[2] The latter phase was accomplished by applying various heat treatment sequences to many coextruded rods, both swaged and unswaged, with various defects in cladding of various thicknesses showing assorted degrees of bonding to the core. The rods were tested for either high temperature aqueous corrosion resistance, uranium concentration in surface layers, effects of radiation on dimensions and corrosion life, bond strength, and several other properties. In an important advance beyond the work of Levine and Lamartin, the diffusion anneal technique was applied to rods with defective cladding made by extrusion of defected cladding components. The results of the above studies were expected to be of value for determining the usefulness and applicability of the technique and also for understanding a mechanism of corrosion protection.

Knowledge of the mechanism would simplify the choice of other fuel elements which might benefit from a diffusion anneal, even when the core was not a uranium-zirconium alloy. A mechanism which appears plausible in view of present results will be discussed in the following report.

III. PROCEDURE

A. Specimen Types

Achievement of the above objectives necessitated the use of corrosion, analytical and metallographic specimens as follows:

Type 1. Corrosion, for studying the effect of the diffusion anneal on rods with:

a. Drilled hole defects in circumferential cladding of various thicknesses.

b. Pre-extrusion defects

(1) In integral end seals.

(2) In circumferential cladding of various thicknesses.

Type 2. Analytical, for determining the uranium concentration in the surface layers of cladding of various thicknesses.

Type 3. Miscellaneous, for studies of

a. Microstructure

b. Microhardness

c. Bond

B. Stock

Coextrusion of Zircaloy-clad U - 2 ^{w}/o Zr provided either integrally end-sealed specimens or rods from which the other kinds of specimens could be made.[3] The stock used for all the extrusions was reactor grade Zircaloy-2 for cladding and nominal U - 2 ^{w}/o Zr for cores. The Zircaloy underwent preliminary extrusions before its final use as cladding components. Both as-cast and prior-extruded U - 2 ^{w}/o Zr were used, after their composition was checked by chemical analysis of the original castings. Actual zirconium contents ranged from 1.7 to 2.4%.

Some of the rods were extruded with integral end seals; other were not. Generally, the former rods were extruded at 1210^{o}F from a 1-5/8 inch liner through a 0.324-inch die. The extruded rods were pickled to remove

the copper remaining from the can which held the billet under vacuum and which acted as a lubricant during extrusion. Each rod was then swaged from a diameter of about 0.300-inch to a diameter of about 0.295-inch. A few integral end-seal rods and all the remaining rods were extruded at 1150°F from a 2-inch liner through 0.400, 0.350, or 0.325-inch diameter dies and most of these were pickled and swaged to a final diameter of about 0.300 inch. All the rods with integral end seals were made with composite cores so that the final rod could be cut into two or more specimens with integral end seals. After swaging (if any) all rod stock was bright etched.

C. Specimen Preparation

The individual specimens were made from the finished rods as follows:

Type 1. Corrosion Specimens

a. Specimens With Drilled Hole Defects

(1) 30-mil Cladding

Corrosion specimens with welded end seals were made from 1.5-inch lengths of rods extruded without end seals. The uranium-zirconium alloy exposed at the ends of these short specimens was bored out to form a hole about 1/4-inch deep with a nearly flat bottom and uranium-free Zircaloy walls. End plugs of Zircaloy-2 were machined to fit snugly in these holes and to extend about 1/32 inch beyond the specimen ends when seated on the hole bottoms. These plugs were degreased and Heliarc welded in place to form the completed test specimen.

Cladding defects were made by drilling holes through the cladding near the mid-length of the specimen. Some of these holes barely entered the core while others were drilled as much as 10 mils into the core. Since the cladding thickness varied slightly from specimen to specimen, the holes were generally drilled to a depth equal to the cladding thickness plus the desired penetration of the core. The actual drill penetration was shown

by a dial micrometer attached to the drill. The cladding thicknesses of most of the specimens were obtained by averaging the thickness of a cladding cross-section at each end of a longitudinally scribed line on each specimen. The actual measurements of thickness were made with a toolmaker's microscope. Several sets of specimens were drilled with a constant force to feed the drill into the specimen. When properly adjusted, the drill would show a marked change in drilling rate at the moment the cladding was pierced and the drill hit the core material. The depth of the drilled hole provided a measure of the cladding thickness of these specimens. When specimens were defected after heat treatment, the hole depth was determined by the pre-treatment cladding thickness plus the desired penetration of the core with proper allowance for the width of the diffusion zone.

Some corrosion results indicated that faulty end-seal welds might cause corrosion failure. Thereafter, specimens with faulty welds were eliminated by short corrosion tests prior to drilling the holes. This test eliminated ambiguity in interpretation of the results of final corrosion tests.

Many of the drilled hole defects were cleaned and examined under a microscope fitted with a dial micrometer, and thereby serving as an optical depth micrometer. This procedure was used to check the hole for depth and cleanliness both before and after heat treatment.

The lengths and diameters of many of these specimens were also measured several times both before and after various heat treatments. The effect of the heat treatment on average length and diameter of each specimen was then determined.

(2) Thin Clad (Machined)

Specimens with thinner cladding were made from some of the above 30-mil clad specimens with welded end plugs. Annular layers of cladding were removed until diameter measurements indicated that the remaining cladding was of the desired thickness. Only the middle 3/4-inch of length was machined; no cladding was removed along a distance of

3/8 inch at each end. Rods made in this way were defected either before or after heat treatment, with the same techniques as for the other 1.5-inch long specimens.

(3) Thin Clad (Extruded)

A few specimens were extruded with approximately 7.5-mil thick cladding and integral end seals. They were then defected in the same manner as the 1.5-inch long specimens.

b. Pre-extrusion Defected Rods

Many rods with so-called "pre-extrusion" defects were prepared for this work. As the name implies, these specimens had cladding defects which resulted from some flaw or treatment given to the cladding components prior to extrusion. These defects and their preparation are discussed in the following paragraphs.

(1) Defective Integral End Seals

(a) Bond-line Corrosion Path

A few specimens with integral end seals were made by extruding end-seal components which had been heated in air until a black coating formed. This was done in an effort to produce a path along the bond line between the cladding and the end seal along which the corrodant might reach the core.

(b) Uranium End Defect

A simulated defective Zircaloy end seal was also attempted by plugging a 0.035-inch axial hole with 0.034-inch diameter uranium wire. This wire formed a 7 to 8-mil diameter thread through the end seal from exposed end to core material when extruded.

(2) Circumferential Cladding Defects

Most of the pre-extrusion defects were made by drilling holes in the Zircaloy sleeve, which was then coextruded to form the circumferential cladding of 5, 10, 15 or 30-mil thickness. These holes

were made with diameters ranging from 26 to 70 mils. They were either extruded as drilled or were plugged with 34-mil uranium wire, 26 and 56-mil corrodible zirconium wire, ZrO_2 powder, or ZrO_2 plugged zirconium capillary tubing. Except for a few rods with ZrO_2 or uranium threads through the 30-mil cladding, these rods were all integrally coextruded at 1210°F to a 24X reduction. The excepted specimens were provided with welded end closures after a 32X reduction at 1150°F.

A few rods with both end seals defective were cut in half and two samples obtained by providing welded end closures where uranium alloy had been exposed.

Type 2. Analytical Specimens

A series of specimens was prepared without defects but otherwise similar to the 1-1/2 inch long specimens with 5, 10, 15 or 30-mil cladding and welded end plugs. These specimens were used for determining whether various diffusion treatments caused significant amounts of uranium to reach the surface of the cladding of various thicknesses. These rods were all bright etched for 15 to 30 seconds in a 5 $^{v}/o$ HF, 45 $^{v}/o$ HNO_3, 50 $^{v}/o$ H_2O solution and rapidly prepared for heat treatment with care to avoid contaminating the freshly etched surface. After heat treatment, the surface along a distance of 7/16 inch from each end was coated with wax and the samples again etched so that only the center 5/8-inch length of surface was attacked. The etched Zircaloy surface was directly above the core material during heat treatment. The etching solution was then analyzed fluorimetrically to give uranium content. The specimens were weighed before and after the pickling step. The weight loss thus determined was used both to calculate the uranium concentration and to estimate the thickness of the layers removed. A low precision ($\pm$ 100 ppm) resulted in large part from the small size of the samples. Larger samples would decrease the error.

Type 3. Miscellaneous

Specimens for metallography and bond test were obtained either from bare-end rods of the same type used for corrosion specimens

or from end-plugged corrosion type specimens. Generally, a bare-end rod from 1 to 1-1/2 inches long was used for studying the effects of a heat treatment on bond, microhardness, or microstructure.

D. Preparation for Heat Treatment

Most specimens were prepared for heat treatment by a thorough degreasing; first in trichloroethylene, then in reagent grade CCl_4. Weld-tested specimens were first wire-brushed at the ends, then polished bright with fine abrasive paper. Attempts to use solvents other than CCl_4 for final cleaning were unsatisfactory. Tantalum foil similarly degreased was wrapped around such specimens. The clean, tantalum-wrapped specimens were placed in quartz or Vycor tubes which were then evacuated and outgassed. The tubes were sealed off for static vacuum heat treatments when a vacuum of about 0.01 micron was obtained. Some specimens were heat treated in a dynamic vacuum where the pressure briefly rose to about 0.3 micron shortly after the start but dropped to about 0.01 micron by the end of a treatment.

E. Heat Treatments

Heat treatments of short rod sections were made with the temperature of the specimens within $5^{\circ}C$ of that desired. Heat treatments of the long rods were made with the temperature within $10^{\circ}C$ of that desired. Treatments were carried out by placing the tube containing the specimens in the furnace with the mid-lengths of the specimens at the middle of the hot zone. A thermocouple was placed with the hot junction at the mid-length of the specimen and against the specimen tube. When the temperature indicated by this thermocouple was in the desired range, timing was begun. In this manner diffusion anneals were performed at 800, 850, 950, 1050, and $1100^{\circ}C$, and supplementary heat treatments at 500, 650, 690, 750, and $800^{\circ}C$.

Cooling was usually accomplished by removing the evacuated tube from the hot furnace and letting it cool in air with contents still in vacuum.*

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*Henceforth this procedure will be described simply as air cooling.

The few water quenches were accomplished by breaking the tube under water immediately after removal from the furnace. Furnace-cooled spcimens were left in the evacuated containers in the furnace after the power had been shut off following the completion of the diffusion anneal stage of the heat treatment. The cooling rate thus obtained averaged about 3^{o}C/min between 800 and 550^{o}C.

F. Corrosion Tests

1. Autoclaves

Corrosion tests were performed in stainless steel autoclaves containing pressurized distilled water at 500, 600 or 650^{o}F. The autoclaves were purged of air by release of steam before operating temperature was reached.

Tests were also made in 750^{o}F, 1500 psi steam after similar purging.

2. Corroded Defect Inspection

Many of the intact corroded specimens were sectioned at the defects which were then examined visually to:

a. Make certain that the defect permitted corrodant to reach the core.

b. Determine the progress of corrosion.

G. Metallography

1. Microstructure Studies

Standard metallographic techniques were generally used. Examination of microstructures was made under bright and polarized light. The specimens were prepared by careful polishing followed by electropolishing with an H_3PO_4 solution.*

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* 5 parts ethylene glycol
10 parts orthophosphoric acid
8 parts ethyl alcohol
6 volts, 20 seconds

2. Microhardness

Microhardnesses were measured on a Tukon microhardness tester having a 50 gram load.

3. Bond Tests

a. Chisel Bond Test

Two methods of bond testing were used. The simplest and most informative was a "chisel bond test" made on a 1/4-inch long piece of clad rod. The section was cut along a diameter until the thickness of uncut core approximately equalled the thickness of the cladding. By wedging action, the specimen was split at the bottom of the cut. The degree of separation of core and cladding at both sides of the break was a qualitative indication of the strength of the bond between the core and the cladding (Fig. 2).

b. Tensile Bond Test

The other bond test, which was used successfully only on unannealed rods with weak bonds, was merely a form of tensile test. A Zircaloy stud was welded to an island of cladding surrounded by bare core. The stud and the specimen were fastened to opposite platens of a tensile machine and a stress applied until rupture occurred.

H. Irradiation Tests

The following specimens were prepared in the usual manner and shipped to Argonne National Laboratory for irradiation and post-irradiation studies:

No. of Specimens	Defects
4	7-mil holes drilled before 1050°C 2 hr, air cooled.
4	7-mil holes drilled after 1050°C 2 hr, air cooled.
4	None - 1050°C 2 hr, air cooled.
2*	None (bare core) 1050°C 2 hr, air cooled.

*The cladding was removed following the heat treatment.

The irradiated specimens were canned in NaK and irradiated to about 0.08 to 0.1% burnup at about 100°C in the MTR. Post-irradiation corrosion tests were conducted in 550 and 600°F water for short periods of time. Measurements of diameter and length were made before and after irradiation.

Eight additional specimens were prepared for higher burnup. Four were given the 2 hr/1050°C-air cool treatment and four were given a nominal 9 hr/850°C-air cool treatment; because of a defective thermocouple however, the latter was actually closer to 830°C. All of these specimens contained 7-mil diameter holes drilled through the 30-mil cladding before heat treatment.

I. Summary of Procedure

In summary, the general procedure was to heat treat, under vacuum, rods of Zircaloy-clad U - 2 ^{w}/o Zr. Bare-end or undefected specimens were then used for metallographic or chemical tests; end plugged specimens with cladding defected either before or after the diffusion anneal were given 500 to 650°F water, or 750°F, 1500 psi steam corrosion tests which lasted until the rod was either destroyed, partly or totally, or the test had to be stopped because of the time and space requirements. Rods which showed good corrosion resistance were spot checked to make certain the defect had pierced the cladding enough to expose core material to corrosive attack. Similar diffusion annealed specimens were irradiated and tests for dimensional changes and corrosion resistance.

IV. RESULTS

A. Corrosion of Specimens With Drilled Holes

1. Effect of Sizes and Depths

a. Large Diameter Defects

Following the first successful application of the diffusion anneal technique to rods with 7-mil defects,[1] larger and deeper defects were made in specimens with well bonded, 30-mil cladding. Although 2-hour treatments at 1050°C were adequate when the defect was 7 mils in diameter, 16 hour treatments did not reliably prevent failure of rods with holes having diameters of 16 or 31 mils, even when such defects barely pierced the cladding. Delayed failure was generally observed in specimens which contained 16 and 31-mil diameter defects, and were air cooled after heat treatment at 1050°C for 16 hours.

b. 7-mil Diameter Defects

(1) Shallow

Since larger defects were not reliably overcome by heat treatment, 7-mil diameter defects were generally used throughout most of the corrosion tests. Initially these defects were drilled only to pierce the cladding and to stop at or barely enter the core. Defects of this type were made either before or after heat treatment; there was no great difference in effect.

Specimens with such holes were heat treated at 800, 850, 950 and 1050°C for various times to determine minimum times necessary for reliably preventing corrosion failure. The data in Table I show that at the respective temperature, heat treatment times of 24, 9*, 1-1/2 and 1/2 hours are sufficient to provide the core protection against the effect of a 7-

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*Two of four specimens annealed at 850°C for 9 hours, air cooled, then shipped to Argonne National Laboratory, failed pre-irradiation corrosion tests. Subsequent investigation indicated that a faulty thermocouple may have caused the temperature to be about 20°C low during the heat treatment.

mil defect through 30-mil cladding. Treatments at 1100°C were not considered because of the nearness of this temperature to the melting point of the core material.

(2) Deeper 7-mil Defects

As experience was gained in drilling such small holes, 7-mil holes could be made which extended about 10 mils into the core material of specimens with 30-mil cladding. Specimens with holes 5 to 10 mils into the core were heat treated for 1.5 hours at 950°C and air cooled. Rapid failure occurred when these specimens were corrosion tested. Similar specimens were heat treated for 2 hours at 1050°C and air cooled. These showed good corrosion resistance and survived over 1500 hours without failure before being discontinued from test. The corrosion pocket formed at the base of one such defect was found to extend about 15 mils into the core material (Fig. 8). Thus, without a doubt, the core material below the diffusion zone was exposed to corrosive attack.

2. Effect of Swaging

No notable difference in behavior was observed between swaged and unswaged rods corroded for 3000 hours (see Table II). Possibly the minimum effective time for treatment at a given temperature is less for unswaged than swaged rods. The uncertainty of the effect of swaging results from a lack of enough samples to provide a basis for a satisfactory statistical treatment which would perhaps reveal subtle variations.

3. Effect of Thinner Cladding

Corrosion tests of diffusion treated specimens with cladding of various thicknesses less than 30 mils were considered important because of the high cost of Zircaloy as well as from the reactor physics aspects.

The results in Table I show that when the cladding thickness is 10 mils or less, the diffusion anneal treatment does not reliably provide

long-term corrosion resistance. Although some survival of thinly clad rods was generally noted, especially in specimens with cladding 10 mils thick, the corrosion life was generally much less than that of similarly defected and heat treated rods with 15 or 30 mils of cladding.

Some of the specimens with 10 mils of cladding were extremely long-lived (1000 to 8000 hours in 650°F H_2O) even though the defect permitted corrosion to occur in the core material. However, at least four of these specimens had small bulges at the defects before being discontinued from test. When the cladding was only 5 mils thick, the diffusion anneal was even less effective in preventing rapid corrosion failure. Nevertheless, specimens with 5 mils of cladding, after a 2 hr/1050°C-air cool heat treatment frequently survived several hundred to a thousand hours before failure even with defects which entered 5 mils into the core beyond the core-cladding interface. Lesser diffusion anneals, although adequate for rods with 30 mils of cladding, provided less corrosion resistance for rods with cladding 10 mils or less in thickness.

4. Effect of Bond Strength

During the course of this work specimens were prepared from a number of rods in which the degree of bonding between cladding and core ranged from non-existent to excellent. Several such bonds, as determined qualitatively by the chisel test, are shown in Fig. 2. The fractures shown of the unannealed specimens will serve as examples of fracture associated with the types of bonds henceforth referred to as broken, poor, and good. During tensile tests the poor bond ruptured when the tensile pressure was 40,000 to 50,000 psi. Better bonds were stronger than the Zircaloy claddings or studs, which broke first, also at about 50,000 psi. Examples of studs with broken bonds and broken cladding are shown in Fig. 3.

The results of the tests, which show a relation between initial bond strength and corrosion resistance, are shown in Table III. Unless otherwise noted the defects were 7-mil diameter holes drilled through the cladding but not into the core. When the bond was at least fair, no consistent

difference was found in corrosion resistance following diffusion anneals which were barely adequate. However, a difference in behavior did appear when the 16-mil diameter defects were subject to 16 hr/1050°C-air cool diffusion anneal. Defects of this size caused rapid failure when they just pierced the cladding of diffusion annealed specimens with fair bonds. In specimens with good bonds, however, they did not cause rapid failure even when they penetrated the cladding plus a few mils of the core.

Specimens from a rod with the weakest unbroken bond showed a marked difference in corrosion resistance depending on the heat treatment, as shown in the central portion of Table III. Four such specimens with 7-mil diameter defects failed rapidly after receiving the normally adequate 9 hr/850°C - air cool treatment (a borderline treatment) while four similar specimens showed good corrosion resistance after either 24 hr/850°C-air cool or 2 hr/1050°C - air cool treatments.

Similarly defected specimens from a rod whose bond had been broken during swaging prior to heat treatment were not consistently prevented from failing even by a 16 hr/1050°C-air cool treatment.

Results of tests to determine the effects of the pre-heat treatment bond strength on the uranium-zirconium diffusion zone formed by a given diffusion anneal are qualitatively shown in Fig. 4.* It is difficult to attach any significance to the differences in microstructures shown for the various diffusion zones. Each of the three preheat-treatment bond strengths defined in Fig. 2 is represented in Fig. 4. The improvement of bond strength by the diffusion anneal technique can be seen by comparing the chisel test results for the annealed and unannealed specimens shown in Fig. 2. Tensile bond tests also showed that rods with initially poor bonds, from which the cladding could be separated before heat treatment by about 45000 lb tensile stress, became stronger than the cladding which ruptured at about 45000 lb tensile stress after heat treatment.

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*In this picture the cross section of unannealed rods reveal a minor difference in thickness of an intermediate layer which apparently varies with bond strength. Further study of this phenomenon might be of interest.

All bond tests showed that initially weak or broken bonds were greatly strengthened by diffusion anneals. In fact a fair bond could be formed from a broken bond at 1050°C during a treatment as short as 15 to 20 minutes. Longer treatments formed even stronger bonds. The large differences in mean thermal expansion coefficients help to explain this phenomenon. Near 125°C, that for uranium is 14.5 μin./in./°C while that for zirconium is only 5.7 μin./in./°C. (4)

The combined results of bond and corrosion tests indicate that although weak bonds are greatly strengthened even by short diffusion anneals, a strong initial bond is desirable if minimum treatments are to provide reliable corrosion protection.

5. Effect of Irradiation Stability Treatments

a. Furnace Cooling

Once the effectiveness of the diffusion anneal technique had been shown to provide increased corrosion protection, its compatibility with secondary heat treatments for irradiation stability became of interest. One of the first such additional treatments consisted merely of furnace-cooling the specimens from the gamma phase. Several sources recommended such a treatment.(5,6,7) Consequently, many variations of heat treatment culminated by furnace cooling from the gamma phase were tested. These tests have been included in Table IV.

The corrosion results from most of these tests indicated that furnace cooling from the gamma phase, either directly from the diffusion anneal temperature or after subsequent reheating, is detrimental and frequently causes rapid failure of rods which received normally adequate diffusion anneals. Attempts to determine the cause of this failure led to discovery of several pertinent facts:

(1) When specimens air cooled after a normally adequate diffusion anneal were reheated, either for 3/4 hour at 750°C, 1 hour at 650°C, or 1-1/2 hours at 550°C, then air cooled, only those reheated to 650°C failed rapidly during corrosion tests.

(2) When specimens were given a normally adequate diffusion anneal and furnace cooled to 700, 650, or 550°C then air cooled, only those furnace cooled to the lowest temperature failed corrosion tests.

(3) Microhardness measurements (see Table VI) of the specimens air cooled and then reheated 1 hour at 650°C and air cooled again, or those furnace cooled, immediately after heat treatment showed that the cladding was softer than on unannealed, or normally annealed then air cooled, rods.

(4) The effect of thermal history after the diffusion anneal on corrosion behavior was affected by the severity of the diffusion anneal. For example, the 650°C air cool step did not cause failure when it followed a 2 hr/1050°C-air cool diffusion treatment.

A similar effect was observed when the 1/4 hr/800°C-furnace cool retreatment caused failure of specimens which were first diffusion annealed at 950°C for 2 hours then air cooled. The same retreatment did not cause failure of similar specimens diffusion annealed at 850°C for 24 hours or 1050°C for 2 or 16 hours. If, however, the reheat time at 800°C was examined to 1/2 hour the 2 hr/1050°C-air cooled specimens failed.

The anomalous behavior of specimens which received these supplementary treatments can be explained if:

1. A longer time at the secondary temperature produces harmful phases, or phases which on cooling transform to harmful phases (Effect 1).

2. The greater the amount of diffusion occurring during a diffusion anneal, the greater its ability to overcome harmful effects (Effect 2).

3. These two effects are competing for a net effect on corrosion resistance. Thus, the 1/4 hour at 800°C causes failure of the 950°C - 2 hour specimens (Effect 2 outweighs Effect 1). However the 1/2 hour at 800°C causes failure of the 1050°C - 2 hour specimens (Effect 1 is more potent than Effect 2). Also, dominance of Effect 2 can help explain the failure of the 2 hr/950°C-air cooled specimens which contrasts with the survival of the 2 hr/1050°C-air cooled specimens following a supplementary treatment at 650°C.

These considerations suggested that specimens furnace cooled after an extended heat treatment at 1050°C to increase the magnitude of Effect 1 might possibly show good corrosion resistance. A rigorous test of this suggestion was run using specimens with 7-mil diameter holes drilled 5 to 10 mils into the core beneath 30-mil cladding. Three of four such specimens showed good corrosion resistance despite the furnace cooling after 16 hours at 1050°C.

b. Other Supplementary Treatments

Other treatments which may improve the irradiation stability of U - 2 w/o Zr rods consist of quenching from the gamma phase, reheating to 690°C for various times, and quenching.[6,7]

The heat treatments using a 690°C soak as final step before corrosion tests were:

(1) 1050°C 2 hr, air cooled; 690°C 1 week, H_2O.
(2) 1050°C 2 hr, H_2O; 690°C 1 week, H_2O.
(3) 950°C 2 hr, air cooled; 800°C 12 hr, H_2O; 690°C 6 hr, H_2O.

Specimens which received these treatments failed rapidly compared to specimens which received only the diffusion anneals used for the initial steps of these treatments. However, specimens which received the 690°C soak generally survived for longer test periods than unannealed rods.

The specimens diffusion annealed at 1050°C were defected after the final heat treatment; the specimens diffusion annealed at 950°C were defected before the initial heat treatment. Since only one of the latter failed, it might be argued that the failure resulted from quench water hitting the hot core material at the base of the defect. However, similarly defected specimens quenched from 950°C did not fail. Although more complete tests are desired, present evidence indicates that the 690° soak is detrimental to the corrosion resistance of diffusion annealed specimens, possibly for some of the same reasons used to explain the effects of furnace cooling.

6. Cross Sections of Defects

a. Uncorroded

(1) Proof that the automatic drilling technique (p.14) permits the drill to pierce the cladding and stop at the core is shown in Fig. 5.

(2) The formation of the diffusion zone at the bases of some heat treated defects is shown in Fig. 6.

b. Corroded

To ensure that defects permitted corrosion to occur in the core material at the defect bases, many specimens were sectioned at the defects after corrosion tests of various durations and the cross sections were examined for a corrosion pocket in the core. The presence of such a pocket indicated that this core material was exposed to the corrodant and presumably would have failed but for the diffusion anneal. Examination of 38 rods showed formation of a small corrosion pocket in the core material, with but four exceptions. Two of the exceptions had purposely been drilled shallow. Most of these small corrosion pockets were observed in rods with 7-mil defects which had been given anneals known to provide good corrosion resistance, but they were also found in rods with 7-mil defects which showed good corrosion resistance but which had been given less than adequate anneals, such as 7 hr/850°C-air cooled, or anneals known to promote failure such as 24 hr/850°C-furnace cooled. It is also of interest that pockets were found in 10-mil clad rod and rods with 16 and 31-mil diameter defects in 30-mil cladding, all of which had survived long tests. Some microphotos of typical pockets are shown in Figs. 7 and 8.

B. Pre-extrusion Defects

As a further test of the diffusion anneal a series of tests was made using integrally extruded rods with cladding defects which resulted from plugged or unplugged holes placed in the cladding components

prior to extrusion. The cladding thickness of the extruded rods varied from 30 to 5 mils. The object was to find out whether the diffusion anneal technique could prevent corrosion failure caused by small defects which simulated those that might conceivably occur during production. In addition, it was hoped to further test the effectiveness of the diffusion anneal when used on thinly clad rods. A series of corrosion tests was performed on a variety of as-extruded rods with defects of various sizes in the Zircaloy sleeve forming the circumferential cladding. Some of these defects were unplugged, others were plugged with uranium, corrodible zirconium, or ZrO_2. Some tests were also made on rods with axial uranium threads through the end seal or with end seals made from purposely dirtied end-seal components. Most of these defects caused corrosion failure of unannealed rods. Exceptions were the coated end seals and the uranium thread through the end seals. With these tests as a guide, rods were made with the smallest defects which appeared to guarantee corrosion failure. These rods were then diffusion annealed and corrosion tested in 650°F water to give the results shown in Table V. Some slight protection by a 16 hr/1050°C-air cool diffusion anneal is indicated by the results for a rod with a defect resulting from a 70-mil diameter unplugged hole. Most of the defects used were too large, however, to be overcome even by heat treatments which caused diffusion greatly in excess of that usually found adequate for drilled holes. Most of these defects were readily visible. The corrodible zirconium plugged type was least conspicuous, and failed slowly even when unannealed; yet, even this type could not be reliably overcome. The one bright part of the picture is that the diffusion annealed rods with uranium threads in 30-mil circumferential cladding have successfully survived periods greatly in excess of those survived by similar but unannealed rods which failed within 630 hours.

Specimens with uranium threads through the end seals successfully survived 1400 hours unannealed and 800 hours annealed before being withdrawn from test. However, as can be seen in Fig. 24 corrosion had apparently not progressed as far as the core material even in the unannealed rod.

Specimens with end seals resulting from components coated with black oxide to produce a bad bond on extrusion have not failed after 4100 hours in 650°F water, whether annealed or unannealed.

The heat treatment of the 8-inch long, pre-extrusion defected specimens revealed several drawbacks in the use of the higher temperature treatments. The tantalum foil tended to stick to the Zircaloy in spots, the specimens frequently warped in the vicinity of the end-seal core interface, and the specimens frequently warped or, presumably because of their own weight, changed in cross section. The 15-mil cladding of a specimen which survived a short corrosion test after a 16 hr/1050°C-air cool treatment was much more extensively corroded around the core than around the end seals.

C. Microhardness Studies

Lamartin and Levine,[1] using a 25 gram load, found no unusually hard brittle zone from core to cladding across the diffusion zone. The tested portions of cladding were softer than tested portions of the core or diffusion zone. During the present work using a 50 gram load the hardness values for the core, diffusion zone and cladding of Zircaloy-clad rods of U - 2 ^{w}/o Zr were determined for composites with various histories. The heat treatment histories and the ranges of hardness values for four rods are shown in Table VI. These data show that following a 2 hr/1050°C-air cool diffusion anneal, which greatly improves the corrosion resistance, a specimen has a harder cladding than the as-extruded material, particularly near the diffusion zone. The hardness of the core also appears to be slightly increased by the same heat treatment. Diffusion annealed specimens which received the furnace cooling step or the supplementary heat treatment at 650°C, both of which destroy the corrosion resistance provided by an adequate diffusion anneal, had slightly softer cores, softer cladding and slightly harder diffusion zones than the specimen which was air cooled after 2 hours at 1050°C. Measurements should be obtained from specimens whose thermal history differed only in treatments following the diffusion anneal so that a more valid comparison can be made.

D. Dimension Changes

The diameters and lengths of many corrosion test specimens were measured before and after a number of heat treatments. The changes in dimensions caused by various anneals are shown in Table VII.

The diffusion treatment caused an increase in diameter of the order of 1 mil or less and a decrease in length of the order of about 5 mils. There seemed to be no great difference between treatments that did not prevent corrosion failure and those that did.

E. Microstructure

Several aspects of the microstructure, particularly core grain size, may be of interest when a choice of diffusion technique is made. Some examinations were made of the effects of various heat treatments on the appearance of both cores and diffusion layers. The microphotos of the structures encountered are included in this report without a detailed discussion (Figs. 9 through 22). These will supplement those referred to throughout the report and may provide answers to questions concerning microstructures after various heat treatments.

A few facts may, however, be pointed out here as of particular interest.

1. Photomicrographs are available which permit comparison of cores and diffusion layers of specimens which were diffusion annealed for 2 hours at 1050°C and then:

   a. Air cooled (Fig. 16).
   b. Air cooled then swaged 25% (Fig. 21).
   c. Air cooled then swaged 25%, reheated to 800°C for 1/4 hour and furnace cooled (Fig. 22).
   d. Water quenched, reheated to 800°C for 1/4 hour and furnace cooled (Fig. 20).
   e. Furnace cooled (Fig. 18).

2. Additional photomicrographs are presented wnich permit comparison of cores and diffusion layers of specimens which were diffusion annealed for 24 hours at 850°C then:

   a. Air cooled (Fig. 9).
   b. Furnace cooled (Fig. 12).

3. A series of diffusion zones were presented and discussed by Lamartin and Levine[1] and related to the phase diagram of the system uranium-zirconium.

4. Fairly rapid cooling from above 800°C generally resulted in the feathery, basket-weave type of core structure. Slow cooling (furnace) appeared to eliminate the feathery structure.

F. Uranium Concentration

Levine and Lamartin's original studies of the concentration gradients throughout the core and cladding of diffusion treated rods of Zircaloy-2 clad U - 2 w/o Zr resulted in the plot shown in Fig. 23. The data which led to this plot were obtained by machining annular layers of metal at known distances from the original interface. The metal turnings were then analyzed by a fluorometric method for uranium content.

Levine and Lamartin did not investigate as such uranium concentrations in the surface layers of the cladding of diffusion annealed rods. The data which they obtained for the concentration gradients in the bulk of the cladding could not be reliably extrapolated to give values for the low concentrations of uranium generally found in the outermost layers of cladding. Since maximum tolerable values for uranium concentrations near the surface of the cladding are frequently specified by reactor engineers, it was of interest to determine such values for rods having various diffusion anneals.

Values for surface concentrations of uranium in diffusion annealed rods of various cladding thicknesses were obtained by briefly etching rods of various cladding thicknesses and fluorometrically determining the uranium content of the pickling solution. The values obtained are shown in Table VIII. Many of these results are erratic; even an unannealed specimen with 10-mil thick cladding showed 280 $\pm$ 100 ppm of uranium in the outer 0.1 mil of surface. As mentioned earlier, the precision of measurement is only $\pm$ 100 ppm because of the specimen size. One factor which contributes greatly to the low precision of measurement is the machining of the specimen.

The specimens with 5, 10, and 15-mil cladding were made by machining away the outermost 25, 20 and 15-mil cladding layers from specimens with 30 mils of cladding. Eccentric machining of the cladding would lead to relatively thin and thick spots in the cladding. Since the diffusion path at the thin spots would be shorter, the surface uranium concentrations would be much higher than normal. Because of the nature of the diffusion phenomenon such localized high uranium contents would not be offset by low values from the thicker cladding and would cause the apparent value for the uranium content of the entire surface to be high. Such an effect would be especially noticeable when the cladding was as thin as 5 mils. If the values for the unannealed rod are used as a blank to correct the other values, the 850°C 9 hr treatment could be considered to cause no uranium to reach the surface of cladding 10 mils or greater in thickness. All other treatments caused a considerable amount of uranium to reach the surface (Table VIII).

G. Irradiation Tests

In the first set of nine specimens, one was unclad, four were clads without defects, and four had 7-mil diameter defects drilled to pierce the clad and only barely enter the core. These were irradiated at about 100°C to give 0.08 to 0.1% burnup of total atoms. Irradiation, evaluation and corrosion tests were performed at Argonne National Laboratory.* Prior to irradiation all the specimens had been annealed at 1050°C for 2 hours, then air cooled. The irradiation-caused dimensional changes are listed in Table IX.

The results for No. 9, the unclad sample, are uncertain because of warping and fine roughness on the surface. The diameter decreases observed on most of the clad rods could be evidence of a strong clad-core bond.

All defected specimens, two with holes made before and two with holes made after the heat treatment, showed good post-irradiation corrosion resistance in 550°F and 600°F water at ANL.[8,9] It should be noted however,

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*Irradiation and corrosion tests at ANL were performed by Karl Smith, Sherman Greenberg and their associates.

that these specimens were also corroded at ANL prior to irradiation; hence, the results, although encouraging, are not conclusive, since the defect may have been plugged before irradiation.

Upon receiving such promising results from the initial irradiation tests, additional diffusion annealed specimens with 7-mil defects through 30-mil cladding were shipped to ANL. Two of these failed pre-irradiation corrosion tests. These were specimens which supposedly received the 9 hr/850°C-air cool treatment but were actually treated at 830°C rather than 850°C because of a tardily discovered defective thermocouple. Since the 850°C 9 hour treatment is a borderline treatment, these specimens would be expected to have inadequate corrosion resistance. No results from these latest irradiation tests have yet been received.

Irradiation of specimens that have been diffusion annealed, then either furnace cooled from the gamma phase or quenched from a 690°C soak for irradiation stability, seems inadvisable since treatments of this type destroy corrosion resistance.

H. Mechanism

One of the objects of this project was to determine the manner by which the diffusion anneal improved the corrosion resistance of Zircaloy-clad rods of U - 2 w/o Zr. Several tentative explanations were mentioned earlier in this report, and in others.[1,2,] The present evidence indicates that bond strength, cladding stiffness and self-compaction of UO_2 combine to give good corrosion resistance. Diffusion treatments which prevent corrosion failure also increase both bond strength and cladding hardness. These increases may be enough to prevent the separation of cladding from core which occurs in untreated rods (see p.10) as corrosion failure progresses. The area in which direct core corrosion occurs is thus restricted to the base of the defect only. Further corrosion of core material could be retarded if the initial corrosion product was self-compacted enough to prevent direct attack of fresh core material by corrodant. Subsequent corrosion would then occur by a process similar to diffusion through a sound oxide layer. Results which support this hypothesis are discussed below:

1. The role played by cladding stiffness is indicated by the following results:

a. There is an increasing tendency for failure to occur as cladding becomes thinner, and therefore weaker.

b. The cladding can be hardened and strengthened by the uranium which diffuses into it. Amounts of uranium as low as 22 $^{w}/o$, such as may occur 4 mils into the cladding nearest the diffusion zone, can harden and stiffen zirconium.[10] Even 10 $^{w}/o$ U makes zirconium three or four times stronger at 600^{o}F.[11] Hardening of the cladding in this region was observed in a specimen which received an adequate diffusion anneal. Nearer the surface the cladding was as soft as in an unannealed rod, as was shown by traverses across the cladding and diffusion zone while obtaining the data for Table VI.

c. Furnace cooling treatments which caused failure of diffusion annealed specimens also caused a general softening of the cladding (see Table VI).

2. The role played by the bond strength has been demonstrated in part by the dependence of diffusion treatment effectiveness on the initial strength of the bond between the Zircaloy and the core material.

3. Evidence that the corrosion is restricted to the base of the defect was obtained by examining cross sections of the corroded defects in 38 specimens. Such cross sections in diffusion annealed rods indicated that corrosion was confined to the core material in the immediate vicinity of the base of the defect (Figs. 7 and 8). This product has been metallographically identified as UO_2. Little or no difference in sizes of corrosion pockets was found in diffusion treated specimens defected only to the core and corroded for long or short periods (Fig. 7).

4. Protection of the core alloy by compacted oxide might be indicated by the results of tests which showed that large diameter defects permitted failure to occur more readily than small diameter defects. When

defects are of larger diameter there is less chance that the hole will be plugged by the initial corrosion product, and self-compaction of the corrosion product will therefore be reduced. Elimination of the partially protective, compacted corrosion product would expose the core material to direct corrosive attack and lead to the more rapid failure that was observed. Unfortunately more rapid failure might also result from the fact that larger diameter holes expose larger areas of core material and permit easier removal of corrosion product before it can be compacted. The following test was intended to test the hypothesis of protection by self-compacted oxide.

A coextruded Zircaloy rod about 0.3-inch diameter was provided at its exposed end with an axial core consisting of a 7 to 8-mil diameter uranium thread. This exposed end was corroded in high temperature water and steam. The object of this test was to deliberately restrict, by means of heavy walls of Zircaloy, the UO_2 formed as the uranium corroded and determine whether the corrosion would continue along the thread. Corrosion did progress far into the rod and away from the end exposed to corrodant (Fig. 24). This test also showed that despite the heavy walls of Zircaloy the UO_2 thread was about 4 mils wider than the uncorroded uranium. The prevention of corrosion by confinement and self-compaction of the initial oxide is, at least for pure uranium, unlikely. One objection to this test is that the corrosion behavior and density changes involved are not the same for pure uranium as for U - 2 ^{w}/o Zr.

5. The Role of Corrosion Resistance

As stated previously, the improvement in corrosion resistance effected by the diffusion anneal cannot be explained simply as a result of the formation of highly corrosion resistant core material. Confirmation of this fact was obtained by the actual observation of corrosion product 15 mils into the core after nearly 1000 hours corrosion of specimens with deep, 7-mil diameter holes (Fig. 8). Corrosion failure of similarly defected specimens occurred following heat treatments which were milder yet capable of preventing the corrosion failure of specimens defected

only to the core. Perhaps this difference in corrosion behavior indicates a dependency of corrosion behavior on the thickness of the interdiffusion zone, or the thickness of the layers of moderately corrosion resistant alloys formed in the portion of the diffusion zone which was originally the U - 2 ^{w}/o Zr alloy. Alloys located in that part of the diffusion zone created by the diffusion of zirconium into the core alloy corrode more slowly than the original core alloy. However, they corrode rapidly compared to unalloyed Zircaloy or zirconium-uranium alloys containing less than 40 to 60 ^{w}/o U.

The zirconium which diffuses into the core material near the bond line may, as Burkart and Lustman suggest,[16] act as a getter for hydrogen liberated during the corrosion process. According to these authors, the discontinuous failure of gamma phase uranium alloys occurs when hydride precipitated at grain boundaries becomes excessive. Hydrogen gettering agents (such as zirconium) might delay the advent of discontinuous failure by preferentially absorbing hydrogen produced by the reaction of uranium and water. Corrosion would then proceed continuously at a rate which is comparable to that observed during air oxidation. Presumably a point would be reached at which the zirconium would become saturated with hydrogen, at which time uranium hydride formation would begin, leading eventually to discontinuous failure. Alternately, swelling of zirconium might occur to the extent that it causes cracking of the base metal.

Whatever the cause a reduced corrosion rate at the bond line can perhaps contribute to the net effectiveness of the diffusion anneal in one or all of the following ways:

1. By eliminating bond line corrosion and minimizing the area of core material exposed to attack.

2. By adding the restraining forces of layers of uncorroded zirconium-uranium alloys to the restraining force of the cladding.

3. By restricting the shape of the initial corrosion pocket and thus redirecting the forces exerted by the original corrosion product so that they act to compact the corrosion product rather than to separate the core and the cladding.

4. By retarding the progress of corrosion sufficiently to permit the formation of a compacted oxide.

If the above hypothetical mechanism helps to explain the beneficial effect of the diffusion heat treatment, perhaps it can also help explain the detrimental effects of furnace cooling or supplementary heat treatments. As mentioned earlier, the failures of some specimens can be explained if some action occurs, during the supplementary heat treatment or furnace cooling step, to offset the diffusion anneal. The failure of so many furnace cooled, diffusion annealed specimens was first thought to result from some phenomena occurring in the diffusion zone. Furnace cooling might cause corrosion failure by decreasing the corrosion resistance of the material which comprises the core and that part of the diffusion layer which was originally part of the core. This is improbable however, since, as mentioned earlier, the alloys in these regions are known to have fairly high corrosion rates following a normally adequate diffusion anneal. This is perhaps indicated by the gradual increase in diameters of the corroded defects as the depth progresses through the diffusion zone (Figs. 7 and 8). In addition, the high temperature aqueous corrosion resistance of Zircaloy, or those alloys that occur in the portion of the diffusion zone initially Zircaloy, is not reduced by various heat treatments to the point where such rapid failure as that observed could occur.[12] Although alloys of 12 ^{w}/o U, presumably furnace cooled from 1000°C, have been reported[12,15] as corroding at about 3×10^{-2} mg/cm^2/hr in 600°F water, this is no worse than the corrosion rate of epsilon phase normally found in the diffusion zone observed in rods annealed in the normal manner.

Another possible explanation of the corrosion failure was that the bond between the cladding and the core was weakened during the slow cooling. Chisel bond tests showed no noticeable separation of cladding, diffusion zone or core (Fig. 2) of specimens given furnace cool treatments known to cause failure of corrosion specimens. Tensile tests showed only that the bond was stronger than the Zircaloy. However, microhardness measurements showed that the cladding and possibly the core of specimens diffusion treated, then either furnace cooled or reheated to 650°C then air cooled, were softer than unannealed or diffusion annealed then air

cooled specimens, but the diffusion zones were slightly harder. The cladding was always softer than the core or diffusion zones.

Since the stiffness of cladding has been considered a major contributor to the successful improvement of corrosion resistance by the diffusion anneal technique, it seems quite possible that a treatment which softens the cladding could partially offset the diffusion anneal effect and cause corrosion failure.

Moreover, furnace cooling from various temperatures (ranging from 700 to 800°C) has been reported[13,14] to decrease room temperature tensile strength and hardness of 10 and 22 w/o uranium-zirconium alloys. Similar weakening of layers of the diffusion zone having these compositions could result from a supplementary heat treatment or furnace cooling following a diffusion heat treatment.

Thus the same mechanism which explains why the diffusion anneal increases corrosion resistance also suggests how furnace cooling or supplementary heat treatment can decrease corrosion resistance by softening and weakening the cladding.

I. Summary

1. The diffusion anneal technique prevents the rapid corrosion failure of swaged or unswaged rods of U - 2 w/o Zr in Zircaloy cladding 15 mils or more thick, pierced by holes of about 7-mil diameter. Failure from larger defects can frequently be retarded by sufficient diffusion treatment. The diffusion anneal usually benefits specimens with thinner cladding but generally does not provide long term corrosion resistance.

Defects of the pre-extrusion type have been successfully overcome by diffusion anneal only when the cladding is 30 mils thick. Little or no improvement in corrosion resistance was observed when the treatment was applied to rods with thinner cladding containing such defects.

2. Furnace cooling or supplementary treatments between 550 and 700°C can cause failure of rods which received otherwise adequate diffusion anneals.

3. Significant uranium increases in concentration were found at the surfaces of rods with 5-mil cladding after treatments of: 9 or 24 hours at 850°C; 1.5 hours at 950°C; 2 hours at 1050°C. Excessive uranium was found in the surface layers of 10-mil cladding after 1.5 hours at 950°C or 2 hours at 1050°C. Little or no uranium was found in the surface layers of 10, 15 and 30-mil cladding after an 850°C 9 hour diffusion anneal.

4. If the minimum diffusion anneals are to give a maximum of protection with a minimum of uranium diffusion to the surface cladding layers, a combination of strong initial bond and cladding more than 10-mils thick is necessary.

5. The shortest treatments found effective for rods with 30-mil cladding are: 800°C - 24 hours, 850°C - 9 hours, 950°C - 1.5 hours, 1050°C - 1/5 hours.

6. The high temperature treatments are undesirable because of the side effects that occur, such as warping of end seals or even sagging or flattening of the specimen, and because of difficulties associated with high temperature heat treatment in vacuo. Moreover, if the time at high temperature is excessive, the corrosion resistance of the cladding is reduced.

7. Irradiation to low burnup (0.1% of total atoms) has slightly affected dimensions of clad, 1-1/2 inch long specimens and appears not to have harmed corrosion resistance provided by a 1050°C 2 hour diffusion anneal. The length change varied from about −27 to 1.9 μin./ppm bu/in. The diameter varied from −6 to 16 μin./ppm bu/in.

8. The key factor needed to fully explain the effectiveness of the diffusion anneal in preventing corrosion failure of Zircaloy-clad rods of U - 2 ^{w}/o Zr has not been identified. The net effect has been found to depend on the interaction of several factors, each of which can either add to or detract from the effective corrosion resistance, depending on the thermal history of the rods. The most important of these factors appear to be:

a. Bond strength
b. Clad strength and stiffness

Other factors which are considered but for which little evidence exists are:

a. Corrosion rate at the base of the defect
b. Formation of a semi-permeable protective barrier of corrosion product between unattacked core and corrodant.
c. Corrosion rate at the diffusion zone.

The most promising factors to study at present are the cladding strength and stiffness. Improvement of these properties might enable the use of a milder diffusion treatment, with the associated reduction of side effects.

9. Cladding is strongly bonded to the core by the diffusion anneal technique even though the original bond is weak or nonexistent.

Table I

High Temperature[1] Water Corrosion of Defected, Diffusion-annealed Specimens

A. 30-mil Thick Cladding, Swaged

Defect Dimensions (mils)		Heat Treatment			Ratio of Number of Failed to Total Number of Specimens Tested During Time Intervals Shown					
Diameter	Depth (2,3)	Temp. (°C)	Hours	Cooling[14]	0-500 (hr)	500-1000 (hr)	1000-3000 (hr)	3000-5000 (hr)	5000+ (hr)	Total of Failures[13]
7	TC	1050	1/4	AC	2/12		0/6	0/4		2
			1/2	AC				0/11	0/1[4]	0
			1	AC					1/2	1
			2	AC			1/66[5]	0/35		1
			2	FC	3/3					3
			2	H_2O					0/1[4]	0
			2	FC to 700°C then AC		0/3				0
			2	FC to 650°C then AC		0/3				0
			2	FC to 550°C then AC	3/3					3
16	TC	1050	1	AC	2/2[6]					2
			16	AC	1/3	1/2			1/1	3
31	TC	1050	1	AC	2/2					2
			16	AC	1/2			0/1		1
7	TC	800	16	AC	1/3		0/2			1
		850	7	AC	8/12		1/4	0/3		9
			8	AC	11/14		1/3	1/2		13
			9	AC			0/24	0/22	0/2	0
			24	AC					0/6	0
			24	FC	9/10			0/1		9
		950	1/2	AC	9/10			0/1		9
			1	AC	3/10			0/7		3
			1-1/2	AC	0/12		0/10			0
			3-1/2	AC					0/2	0
			5	AC					0/2	0
			2	FC	3/3					3
			2	H_2O			0/2			0

Table I.A. (Cont'd.)

Defect Dimensions (mils)		Heat Treatment			Ratio of Number of Failed to Total Number of Specimens Tested During Time Intervals Shown					
Diameter	Depth[2,3]	Temp. (°C)	Hours	Cooling (14)	0-500 (hr)	500-1000 (hr)	1000-3000 (hr)	3000-5000 (hr)	5000+ (hr)	Total of Failures[13]
7	ITC (5-10 mils)	950	1-1/2	AC	7/7					7
		1050	2 16	AC FC	1/4		0/8 0/3			0 1
16	ITC (4.5 mils)	1050	1 16	AC AC	2/2[6]		0/3		0/2	2 0
	ITC (30 mils)	1050	1	AC	2/2[6]					2
31	ITC (4.5 mils)	1050	1	AC	2/2					2

B. 15-mil Thick Cladding[7] Swaged

7	TC	850	9	AC			0/3			0
		1050	2	AC		0/4[8]				0
	ITC (5-10 mils)	1050	2	AC		0/4[8]				0

C. 10-mil Thick Cladding[9] Swaged

7	TC	850	9	AC	2/6	2/4	0/2			4
		950	1-1/2	AC	1/3		0/2			1
		1050	2	AC	1/9	0/6			1/1	2

Table I.C. (Cont't)

Defect Dimensions (mils)		Heat Treatment			Ratio of Number of Failed to Total Number of Specimens Tested During Time Intervals Shown					
Diameter	Depth[2,3]	Temp. (°C)	Hours	Cooling (14)	0-500 (hr)	500-1000 (hr)	1000-3000 (hr)	3000-5000 (hr)	5000+ (hr)	Total of Failures[13]
7	ITC (core penetration unknown)	850	9	AC	2/2					2
	ITC (3-10 mils)	1050	2	AC	1/4[8]				1/3	2

D. 7.5-mil Thick Cladding, Swaged[9]

7	TC	1050	2	AC	1/1					1
	ITC (3.5-4.5 mils)	1050	2	AC	2/2					2

E. 5-mil Thick Cladding[12] Swaged

7	TC	850	9 24	AC AC	3/5	1/2	0/1 2/3			4 2
		950	1-1/2	AC	1/3	1/2	0/1			2
		1050	2	AC	1/4	2/3				3
	ITC (core penetration unknown)	850	9	AC	2/2					2
	ITC (8-10 mils)	1050	2	AC	4/6	2/2				6

TABLE I (Cont'd.)

F. 30-mil Thick Cladding, Unswaged

Defect Dimensions (mils)		Heat Treatment			Ratio of Number of Failed to Total Number of Specimens Tested During Time Intervals Shown					
Diameter	Depth[2,3]	Temp. (°C)	Hours	Cooling (14)	0-500 (hr)	500-1000 (hr)	1000-3000 (hr)	3000-5000 (hr)	5000+ (hr)	Total of Failures[13]
7	TC	800	24	AC					1/4	1
		850	7	AC					0/2	0
			8	AC					0/2	0
			9	AC					1/5	1
			24	FC	5/5					5
		950	1	AC	1/2				0/1	1
			2	AC					0/4	0
			3	AC					0/4	0
		1050	1/2	AC					0/3	0
			2	AC			0/3			0
16	TC	1050	16	AC				1/2	0/1	1
31	TC	1050	16	AC		1/2	1/1			2

(1) Unless otherwise indicated test was conducted in 650°F water. Frequently 500, 600°F water and 750°F 1500 psi steam were used because autoclaves for such tests were available while 650°F test equipment

TABLE I (Cont'd.)

Footnotes:

(1) Unless otherwise indicated test was conducted in 650°F water. Frequently 500, 600°F water and 750°F 1500 psi steam were used because autoclaves for such tests were available while 650°F test equipment was not.

(2) TC - defect penetrated cladding and stopped at core.

(3) ITC - defect penetrated cladding and entered core for distance indicated in parentheses.

(4) Tested approximately 4000 hours in 600°F, H_2O followed by 4000 hours in 650°F, H_2O

(5) Combined 600°F and 650°F, H_2O tests.

(6) 500°F, H_2O only.

(7) Cladding machined to 15-mil thickness from 30-mil thickness unless otherwise stated.

(8) Extruded with 15-mil thick cladding and a fairly strong bond.

(9) Cladding machined to 10-mil thickness from 30-mil thickness.

(10) Tested in 600°F, H_2O only.

(11) Extruded with 7.5-mil thick cladding and integral end seals.

(12) Cladding machined to 5-mil thickness from 30-mil thickness.

(13) The total number of specimens tested is shown by the denominator of the 0-500 hour column.

(14) AC = Specimens were left in evacuated container which was air cooled following the diffusion anneal.
FC = Specimens were left in evacuated container which was cooled within the furnace following the diffusion anneal.

Table II

Comparison of Corrosion Behavior of Swaged and Unswaged, Defected, Diffusion Annealed Rod Specimens with 30-mil Cladding

Defect		Heat Treatment			Ratio of Number of Failed to Total Number Tested After 300 hours in 650°F Water	
Diameter (mils)	Depth	Temp. (°C)	Time (hr)	Cooling	Swaged	Unswaged
7	TC*	850	7	AC**	9/12	0/2
			8	AC	13/14	0/2
			9	AC	0/22	0/5
			24	FC***	9/10	5/5
		950	1	AC	3/10	1/2
		1050	1/2	AC	0/11	0/3
			2	AC	1/66	0/3
16	TC	1050	16	AC	1/2	2/2
31	TC	1050	16	AC	1/2	2/2

*TC = defect was drilled to pierce the cladding but not enter the core.

**AC = specimens were left in evacuated container which was air cooled following the diffusion anneal.

***FC = specimens were left in evacuated container which was cooled within the furnace following the diffusion anneal.

Table III

The Effects of Initial Bond Strength on the High Temperature Water Corrosion of Defected, Diffusion Annealed Specimens

Pre-Treatment Bond Strength*	Defect Dimensions (mils)		Heat Treatment			Ratio of Number of Failed to Total Number of Specimens Tested During Time Intervals Shown					
	Diameter	Depth	Temp. (°C)	Hours	Cooling	0-500 (hr)	500-1000 (hr)	1000-3000 (hr)	3000-5000 (hr)	5000+ (hr)	Total of Failures***
Broken (during swaging)	7	TC	850	16	AC	2/2					2
			950	16	AC	1/2				0/1	1
			1050	2	AC	2/3				0/1	2
				16	AC	2/6		1/4		0/3	3
Fair	7	TC	850	9	AC	5/5					5
				24	AC				0/2		0
				24	FC	2/2					2
			1050	2	AC				0/2	0/1	0
	16	TC	1050	16	AC	1/3	1/2			1/1	3
Good**	16	ITC (4.5 mils)	1050	16	AC			0/3		0/2	0

*See p. 23 and Fig. 2 for descriptions of bond strength.

**Refer to Table I for behavior of other specimens with initially good or excellent bonds.

***The total number of specimens tested is shown by the denominator of the 0-500 hour column.

Table IV

Corrosion Behavior of Defected, Diffusion Annealed Rods of Zircaloy-clad U - 2 w/o Zr After Supplementary Heat Treatments

Supplementary Heat Treatment			Diffusion Anneal			Ratio of Failed to Total Specimens After 1000 hr in 650°F H_2O
Temp. (°C)	Duration (hr)	Cooling	Temp. (°C)	Duration (hr)	Cooling	
550	1-1/2	AC	950	2	AC	0/2
650	1	AC	950	2	AC	6/6
			1050	2	AC	0/4
690	168	H_2O	1050	2	AC	3/3*
690	168	H_2O	1050	2	H_2O	3/3*
750	3/4	AC	950	2	AC	0/2
800	1/4	FC	850	24	AC	0/3
			950	2	AC	3/3
			1050	2	AC	0/3
			1050	2	H_2O	0/1
			1050	16	AC	0/3
800	1/2	FC	950	2	AC	3/3
			1050	2	AC	4/6
800	1/12	H_2O	950	2	AC	1/2
690	6	H_2O		plus		

*These specimens were defected after heat treatment. All other specimens in this table were defected before heat treatment.

Table V

Corrosion of Pre-extrusion Defected Rods in 650°F Water Air-cooled After Heat Treatment

Cladding Thickness (mils)	Pre-extrusion Defect Diameter (mils)	Plug Material	No. of Specimens	Heat Treatment		Results
				Time (hr)	Temp. (°C)	
15	70	unplugged	2	9	850	F**
	70	unplugged	1	15	850	F
	70	unplugged	1	2	950	F
	70	unplugged	1	4	950	F
	70	unplugged	1	8	1050	F
	70	unplugged	3	16	1050	F
10	46.5	unplugged	1	24	850	F
	46.5	unplugged	1	16	1050	F
5	46.5	unplugged	1	24	850	F
	46.5	unplugged	1	16	1050	F
	26	unplugged	1	24	850	F
30	34	Uranium*	3	2	1050	OK 2000-3000 hr
15	34	Uranium*	1	24	850	F
	34	Uranium*	2	16	1050	F
10	34	Uranium*	1	48	950	F
5	34	Uranium*	1	16	1050	F
15	26	Corrodible Zirconium	1	24	850	F
10	26	Corrodible Zirconium	1	2	1050	F

Table V (Cont'd.)

Cladding Thickness (mils)	Pre-extrusion Defect Diameter (mils)	Plug Material	No. of Specimens	Heat Treatment		Results
				Time (hr)	Temp. (°C)	
30	26	ZrO_2*	2	2	1050	F
30	7-8 mil diameter thread through extruded end seal		2	9	850	OK ~800 hr***
			1	48	950	OK ~300 hr***
	Defective end seal bonds		2	2	1050	OK 4100 hr

*Each rod had 8 rather than 4 defects made on the circumference of total extrusion Reduction = 3 2/1

**F = catastrophic failure occurred rapidly.

***Unannealed rods with similar defects did not fail after 1000 hr.

Table VI

Microhardness of the Core, Diffusion Zone Cladding and of Zircaloy-Clad U-2 $^{w}/_{o}$ Zr Rods with Various Heat Treatment Histories

Heat Treatment	Knoop Hardness Number								
	Core			Diffusion Zone			Cladding		
	Max	Min	Av.	Max	Min	Av	Max	Min	Av
As extruded and swaged	510	380	450	-	-	-	220	180	190
1050°C 2 hrs, air cooled	630	390	470	410	310	360	260	200	220
850°C 24 hrs, Furnace cooled	510	300	390	450	360	390	250	140	160
950°C 2 hrs, air cooled then 650°C 1 hr, air cooled	470	300	380	410	340	400	270	130	190

Note: Microhardnesses were determined on a Tukon microhardness testor using a 50 g load.

Table VII

Changes in Dimensions of Zircaloy-clad U - 2 w/o Zr Rods Caused by Diffusion Anneals

(Nominal specimen dimensions: Diameter = 0.3 inch; Length = 1.5 inch)

No. of Specimens Averaged	Heat Treatment			△ Diameter (mils)		△ Length** (mils)	
	°C	Hours	Cooling***	Min	Max	Min	Max
3	800	16	Air	0.3	0.9	−4	+0.5
10	850	7	Air	0.1	0.9	−3.8	+7.2
10	850	8	Air	0.6	1.1	−1.9	+6.9
20	850	9	Air	0.1	1.1	−1.4	−7.6
9	850	24	Furnace	0.4	0.9	−2.0	−7.2
10	950	0.5	Air	0.7	0.9	−2.7	+6.0
10	950	1	Air	0.6	1.1	−3.2	−6.9
10	950	1.5	Air	0.9	1.3	−3.6	−6.8
3	950	2	Furnace	0.6	0.7	−4.5	−6.6

*Difference of average values for 2 sets of 4 readings near mid-lengths.

**Differences of average values for 2 sets of 6 readings each. Roughness at welded ends caused wide variations. The length change may be invalidated by the end plug changes.

***Air cooling accomplished by removing the evacuated tube from the hot furnace and letting it cool in air with contents still in vacuum.

Table VIII

Uranium Concentration at Surfaces of Diffusion Annealed Rods of Zircaloy-clad U - 2 w/o Zr

Heat Treatment		Cladding Thickness (mils)	Uranium Concentration in Outer 0.1 Mil Surface Layer of Cladding (ppm ± 100)
Temp. (°C)	Time (hr)		
850	9	5	ND* to 1900
		10	ND to 270
		15	ND to 260
		30	ND
850	25	5	650 to 980
950	1.5	5	1310 to 2130
		10	ND
1050	2	5	1700 to 1800
		10	900 to 1600
Untreated		10	260 to 280

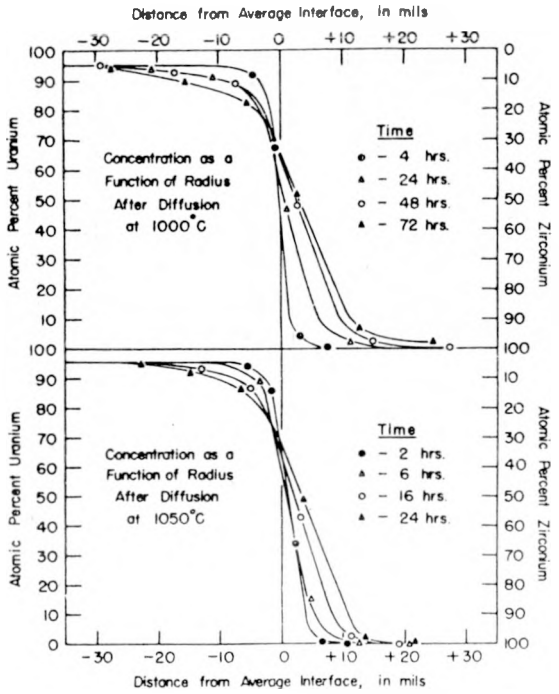
*ND - not detectable by the method used; less than 200 ppm.

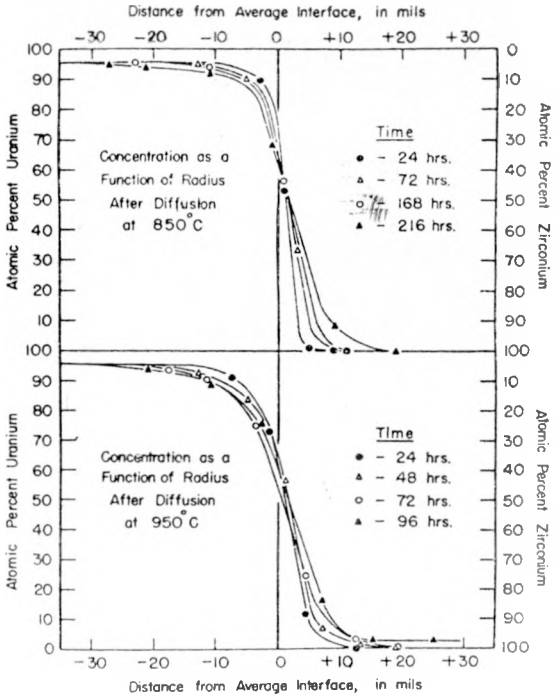
Table IX

Dimensional Changes Caused by Irradiation of Bare or Zircaloy-clad* U - 2 w/o Zr Rods at About 100°C to 0.08 - 0.1% Burnup

	Samples	Length Changes (mils)	Diameter Changes (mils)
Clad	1	24.0	−3
	2	1.9	−3
	3	0.0	−3
	4	−26.6	−2.5
	5	0.0	−3
	6	0.2	+1
	7	0.0	+3
	8	+0.7	−1.5
Unclad (Bare Core)	9	+50.9	2

*Clad thickness is about 30 mils.





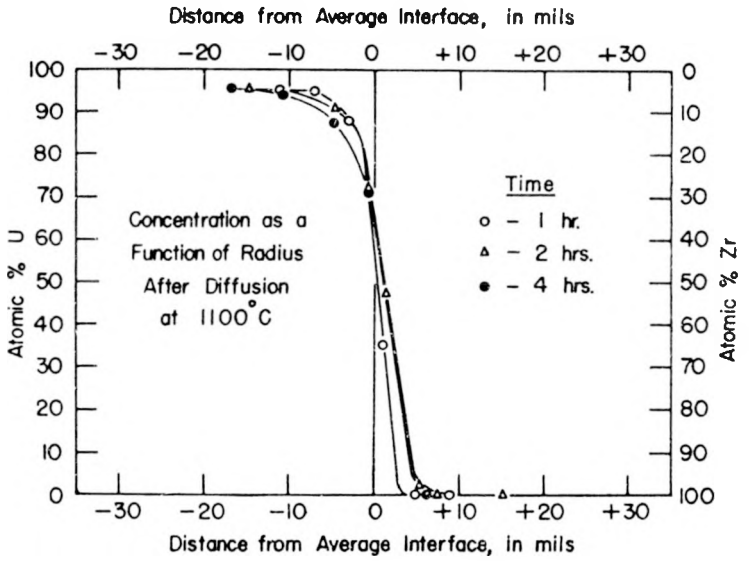
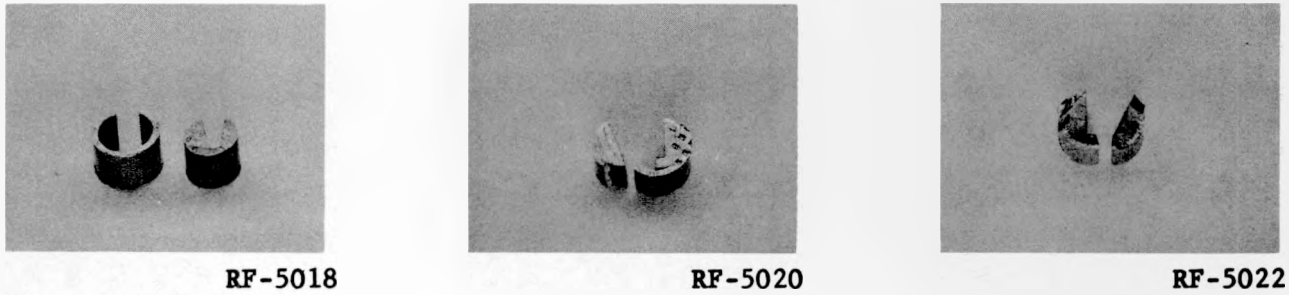
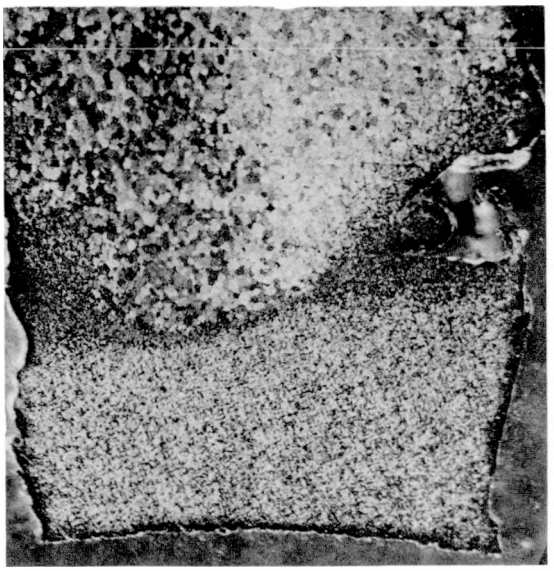


Fig. 1 - Compositions of diffusion zones formed in Zircaloy-clad rods of U - 2 W/o Zr by various heat treatments.(1)



Unannealed	RF-5018	RF-5020	RF-5022
Initial Bond Strength	Broken	Poor	Good (no separation of core and cladding)
Heat Treated	RF-5019	RF-5021	RF-5023
	1050°C - 1-1/2 hr Air cooled	1050°C - 7 hr Air cooled	850°C - 24 hr Furnace cooled

Fig. 2 - Degrees of bonding of Zircaloy-clad to U - 2 w/o Zr core as determined by chisel bond tests on unannealed swaged rods or swaged rods annealed as indicated. Each heat treated specimen had the same bond strength initially as the unannealed specimen shown directly above. Note the improvement caused by the heat treatment.



50X A-925-1

Unannealed specimen. Bond ruptured at core-cladding interface at 45,000 psi tensile stress.

50X A-925-3

Diffusion annealed 24 hr/850°C - furnace cooled. Cladding near surface ruptured before bond at 45,000 psi tensile stress.

Fig. 3 - Tensile bond test studs and specimen cladding after rupture of bond (top) or cladding (bottom) of swaged extruded Zircaloy-clad rods of U - 2 w/o Zr.

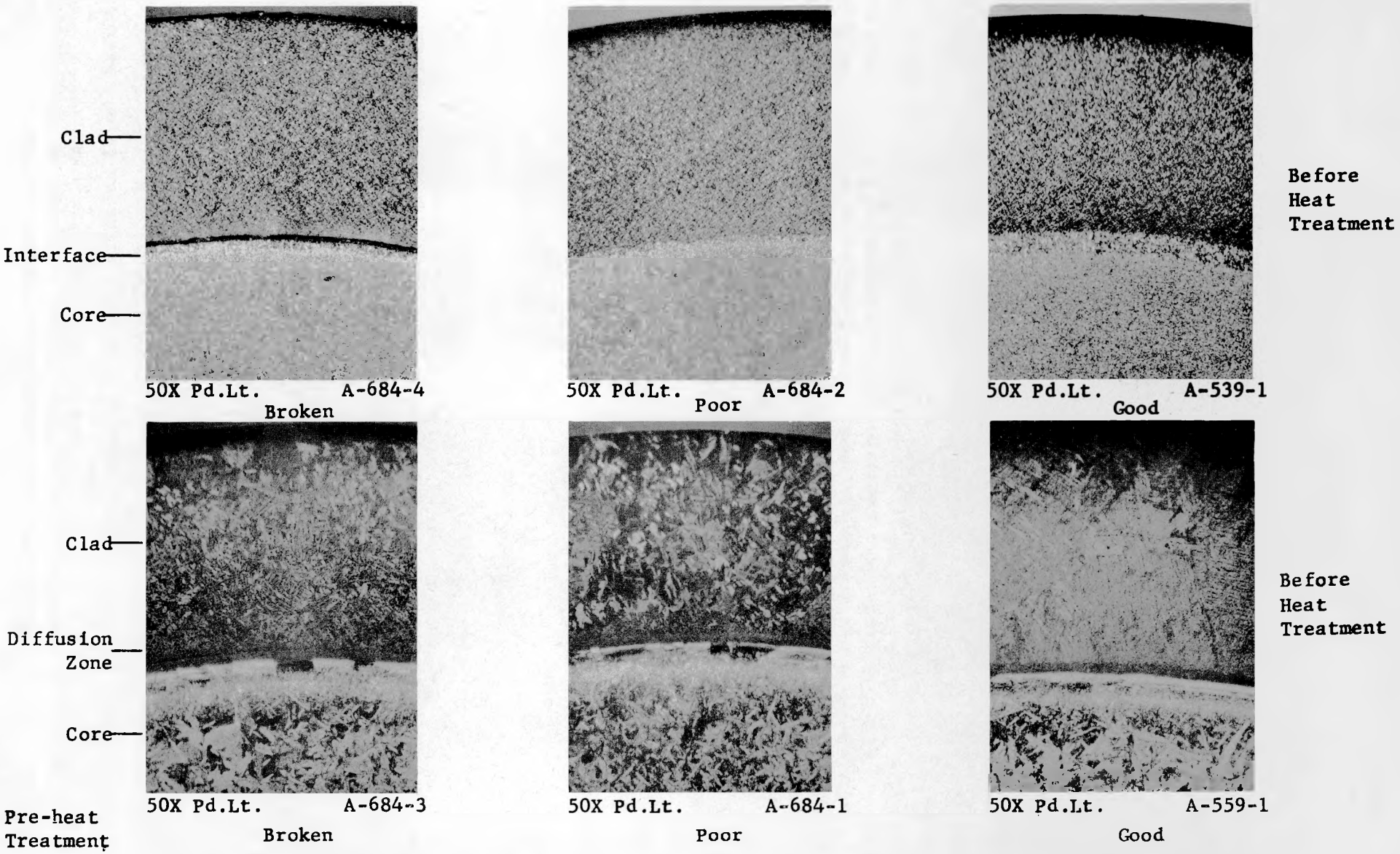
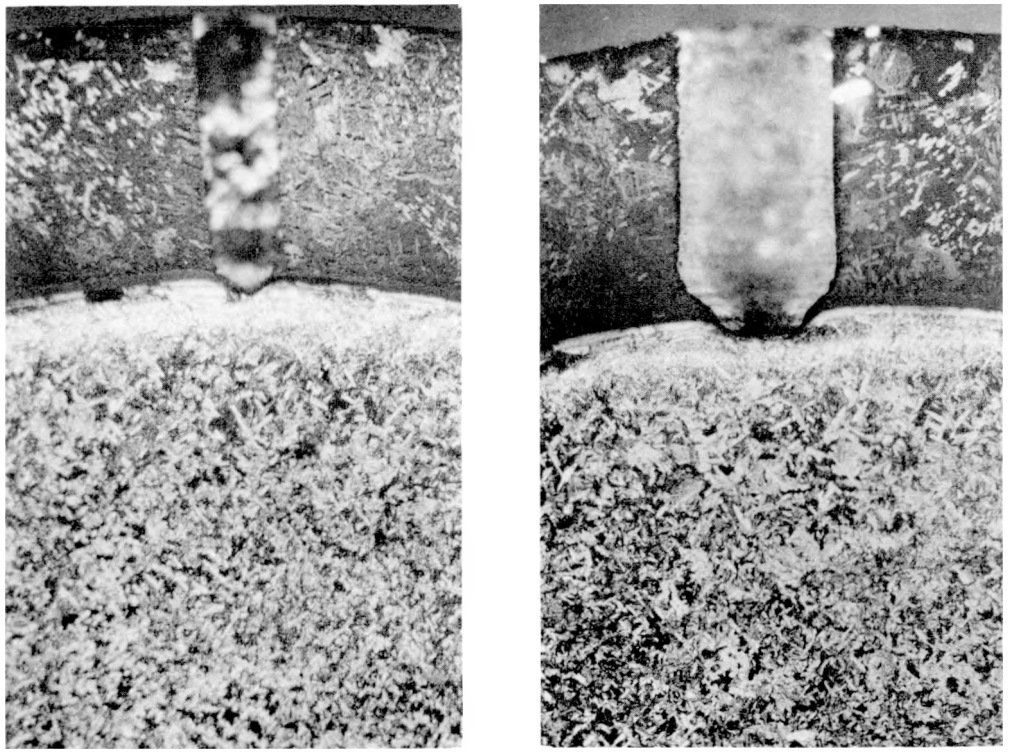


Fig. 4 - Microstructures of swaged rods with core-cladding bonds of various strengths before and after 1050°C - 2 hour - air cool diffusion heat treatments. Note thickening of intermediate zones of unannealed specimens as bond improves.

50X Bt.Lt. RF-4579

Fig. 5 - Transverse cross section of unannealed Zircaloy-clad rod of U - 2 w/o Zr showing 7-mil diameter hole drilled by automatic stop-drilling technique to pierce cladding and stop at core.



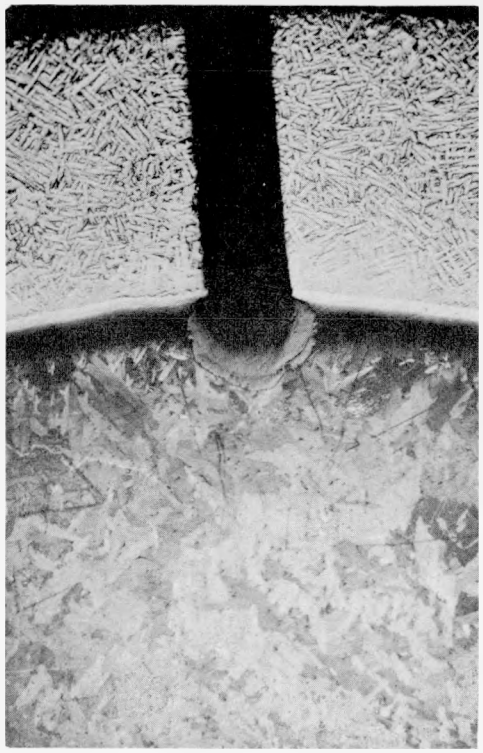
50X Pd.Lt. A-684-9

7-mil diameter defect pierced cladding stopped at core.

50X Pd.Lt. A-684-12

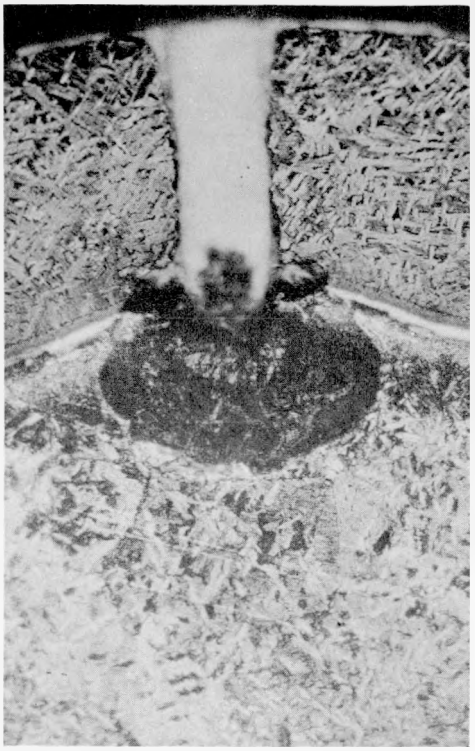
16-mil diameter defect pierced cladding stopped at core.

Fig. 6 - Regions of core, cladding and diffusion zones in vicinity of defects after heat treatment for 2 hours at 1050°C.



50X Pd.Lt. A-583-2(b)

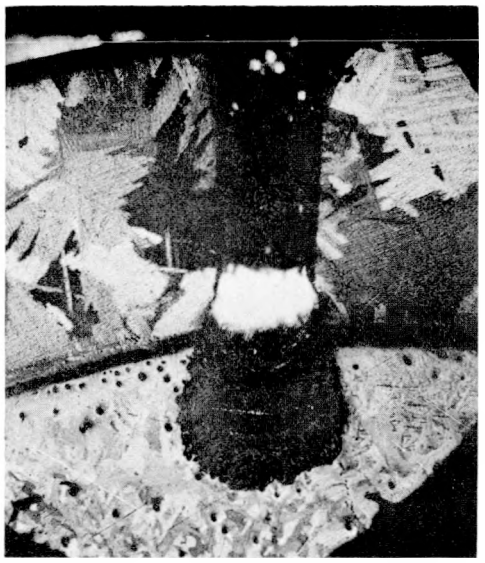
128 hours in 600°F water.



50X Pd.Lt. A-684-8(a)

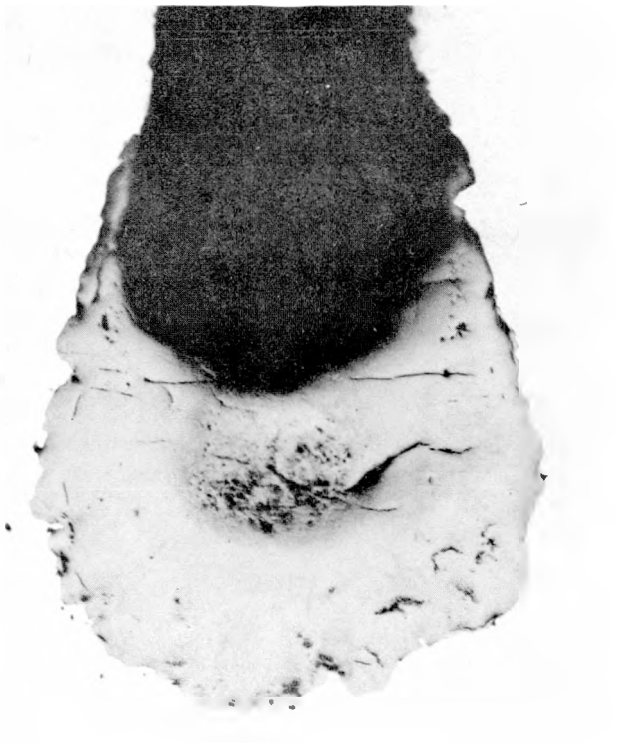
1073 hours in 600°F water, followed by 2700 hours in 750°F, 1500 psi steam.

Fig. 7 - Corrosion at bottoms of 7-mil diameter defects drilled through 30-mil cladding before 1050°C - 2 hour - air cool diffusion anneals followed by the corrosion tests indicated.



50X Pd.Lt. A-1108(b)

(a)

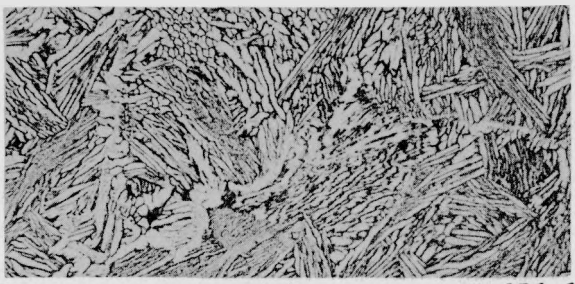


150X Bt.Lt. A-1108(c)

(b)

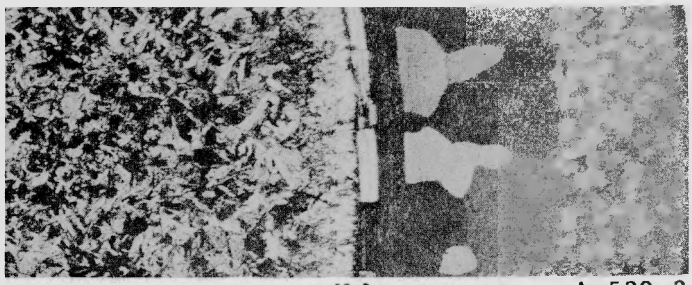
Fig. 8 - Two views of corrosion at base of 7-mil diameter defect drilled 10 mils into the core material below 30-mil thick cladding prior to a 1050°C - 2 hour - air cool diffusion anneal. (a) and (b) show the same defect after 1100 hours in 650°F water.

Core



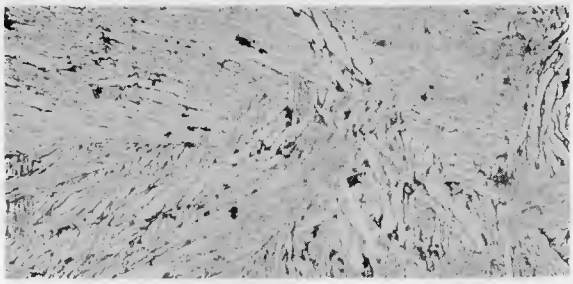
500X Bt.Lt. (a) A-656-1

Core Diffusion Cladding Zone

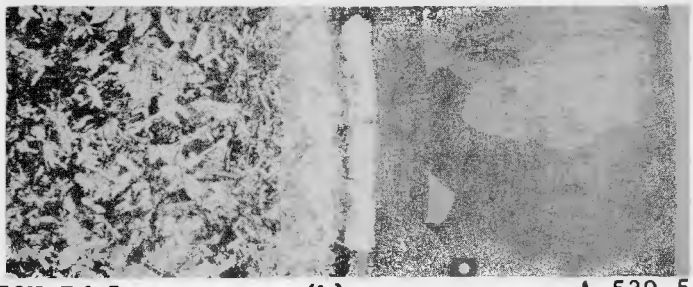


50X Pd.Lt. (b) A-539-3

Fig. 9 - 850°C 24 hr, air cooled.

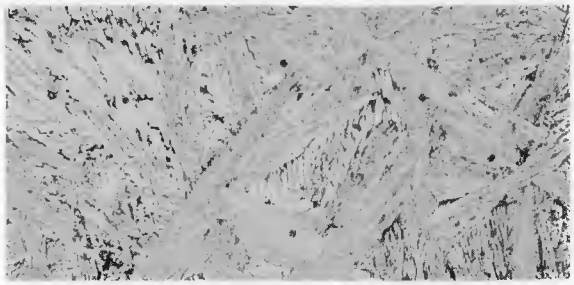


500X Bt.Lt. (a) A-656-2

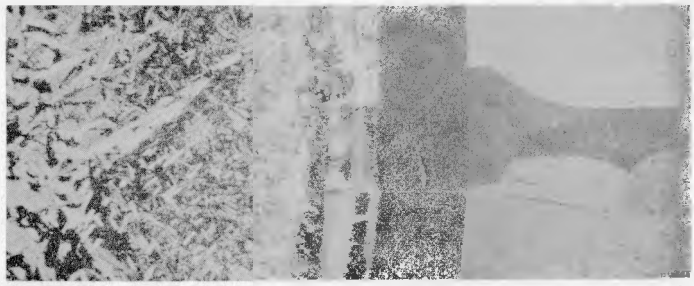


50X Pd.Lt. (b) A-539-5

Fig. 10 - 850°C 72 hr, air cooled.

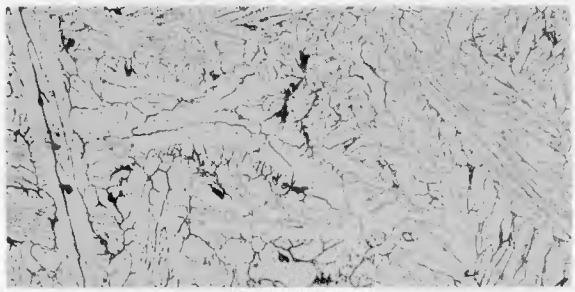


500X Bt.Lt. (a) A-656-3

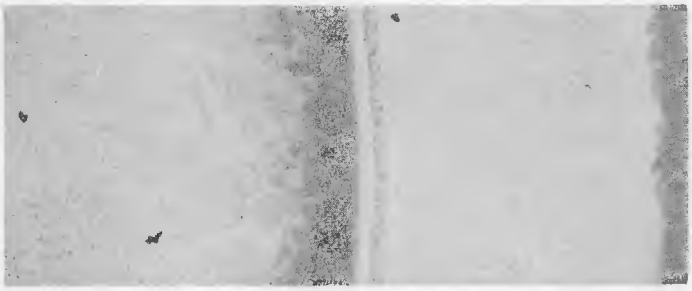


50X Pd.Lt. (b) A-548-1(a)

Fig. 11 - 850°C 216 hr, air cooled.



500X Bt.Lt. (a) A-742-2(b)

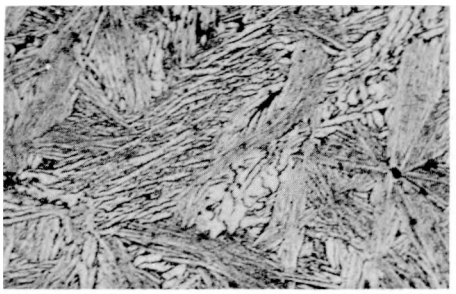


50X Pd.Lt. (b) A-742-2(a)

Fig. 12 - 850°C 24 hr, furnace cooled.

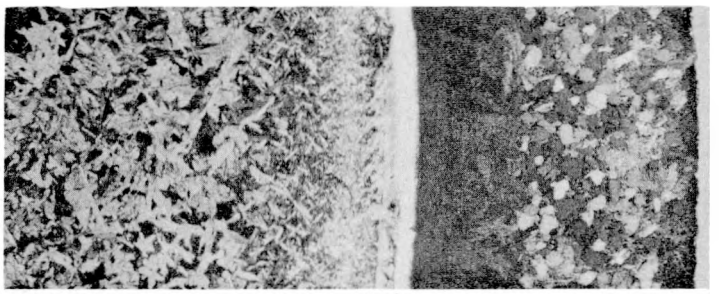
Microstructures of coextruded (1150°F) Zircaloy-clad U - 2 w/o Zr rods after heat treatments listed.

Core



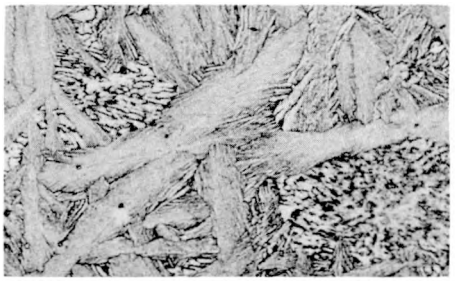
500X Bt.Lt. (a) A-656-4

Core Diffusion Zone Clad-ding

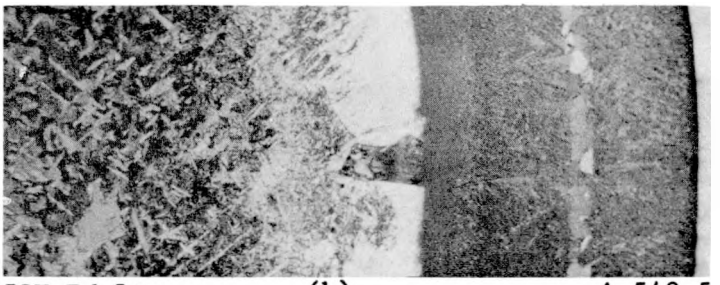


50X Pd.Lt. (b) A-548-2

Fig. 13 - 950°C 24 hr, air cooled.

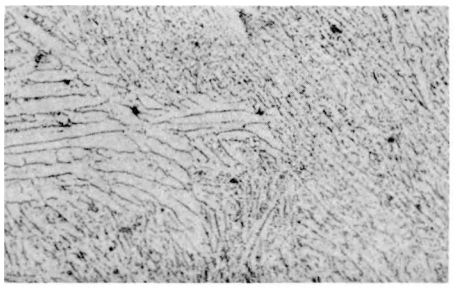


500X Bt.Lt. (a) A-656-5

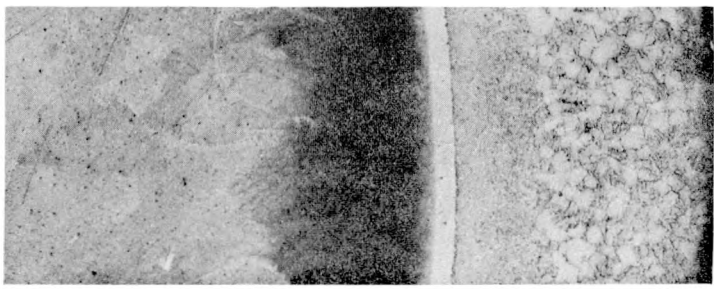


50X Pd.Lt. (b) A-548-5

Fig. 14 - 950°C 96 hr, air cooled.



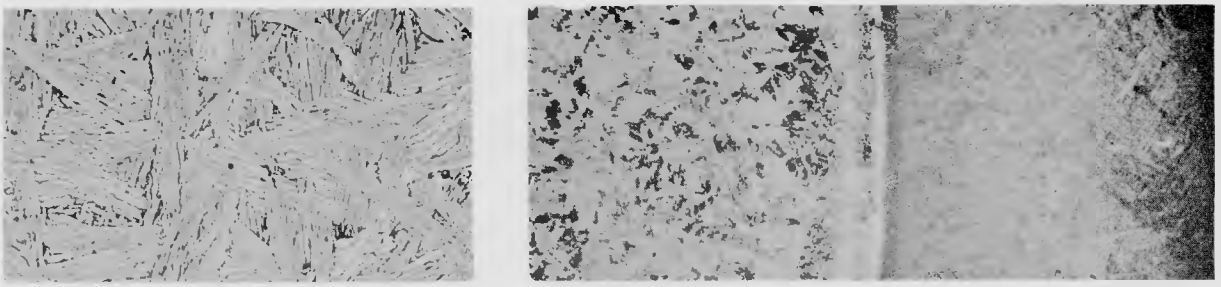
500X Bt.Lt. (a) A-747-2(a)



50X Bt.Lt. (b) A-747-2(b)

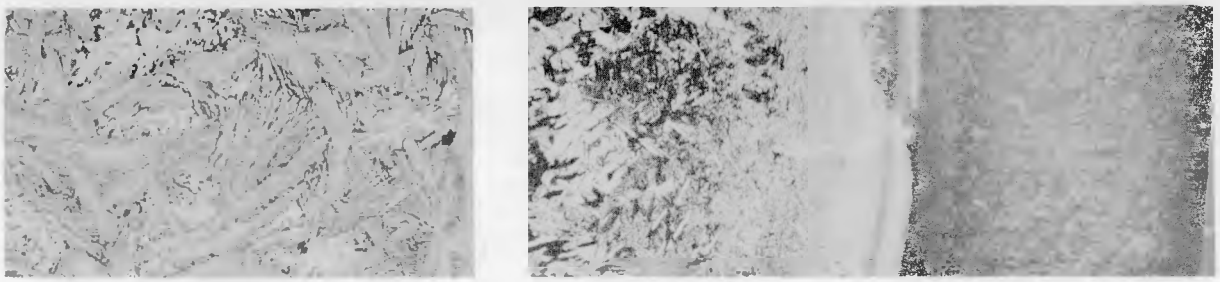
Fig. 15 - 950°C 24 hr, air cooled, plus 800°C 1/4 hr, furnace cooled.

Microstructures of coextruded (1150°F) Zircaloy-clad U - 2 w/o Zr rods after heat treatments listed.



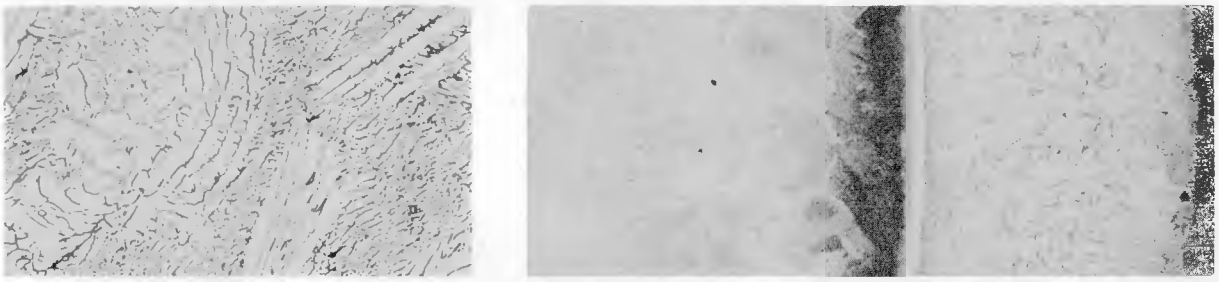
500X Bt.Lt. (a) A-656-6 50X Pd.Lt. (b) A-559-1

Fig. 16 - 1050°C 2 hr, air cooled.



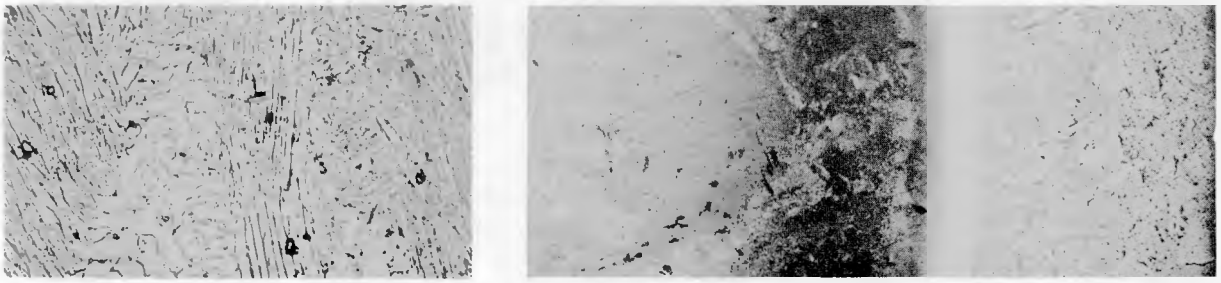
500X Bt.Lt. (a) A-656-5 50X Pd.Lt. (b) A-559-4

Fig. 17 - 1050°C 24 hr, air cooled.



500X Bt.Lt. (a) A-742-1(a) 50X Bt.Lt. (b) A-742-1(b)

Fig. 18 - 1050°C 2 hr, furnace cooled.

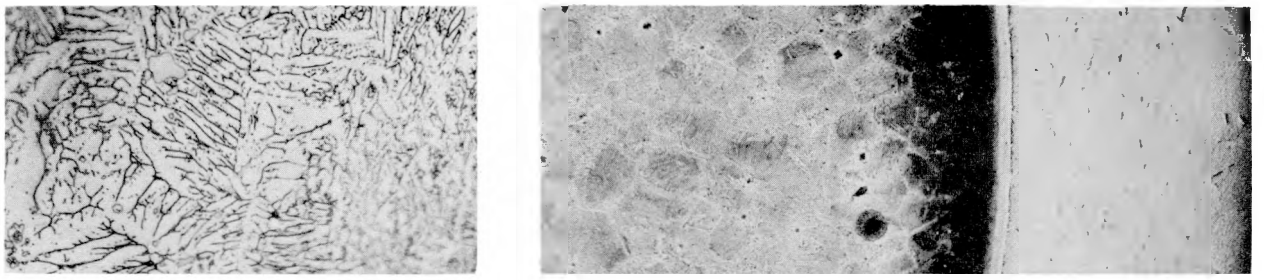


500X Bt.Lt. (a) A-742-3(b) 50X Bt.Lt. (b) A-742-3(a)

Fig. 19 - 1050°C 24 hr, furnace cooled.

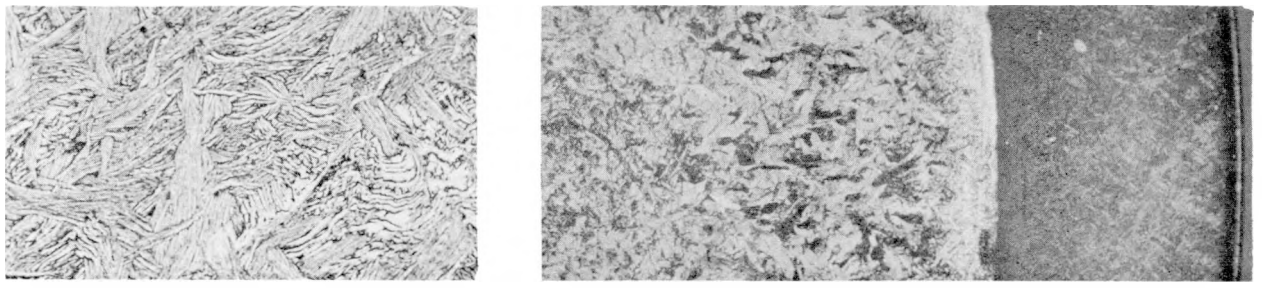
Microstructures of coextruded (1150°F) Zircaloy-clad U - 2 w/o Zr rods after heat treatments listed.

Core Core Diffusion Zone Clad-ding



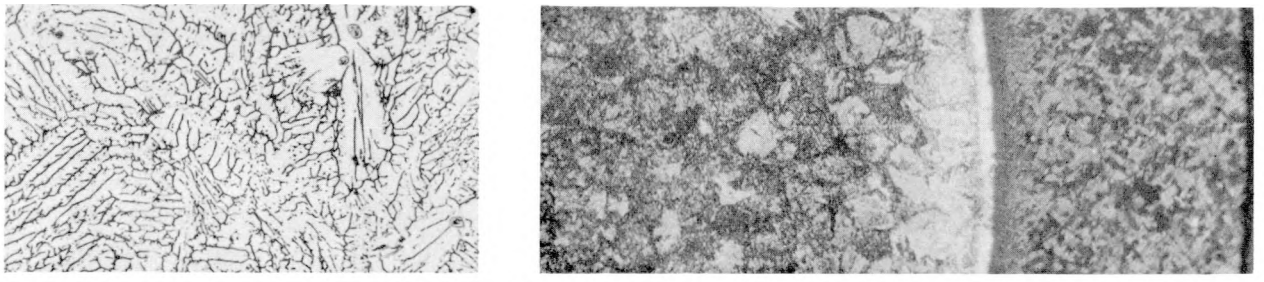
500X Bt.Lt. (a) A-747-3(b) 50X Bt.Lt. (b) A-747-3

Fig. 20 - 1050°C 2 hr H_2O and 800°C 1/4 hr, furnace cooled.



500X Bt.Lt. (a) A-725-1(b) 50X Pd.Lt. (b) A-725-1

Fig. 21 - 1050°C 2 hr, air cooled and cold swaged 25% reduction.



500X Bt.Lt. (a) A-725-4(c) 50X Pd.Lt. (b) A-725-4

Fig. 22 - 1050°C 2 hr, air cooled and cold swaged 25% reduction, 900°C 1/4 hr furnace cooled.

Microstructures of coextruded (1150°F) Zircaloy-clad U - 2 w/o Zr rods after treatments listed.

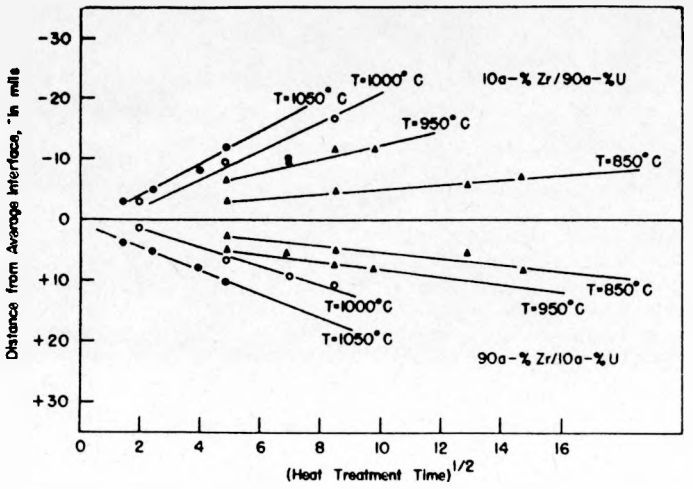
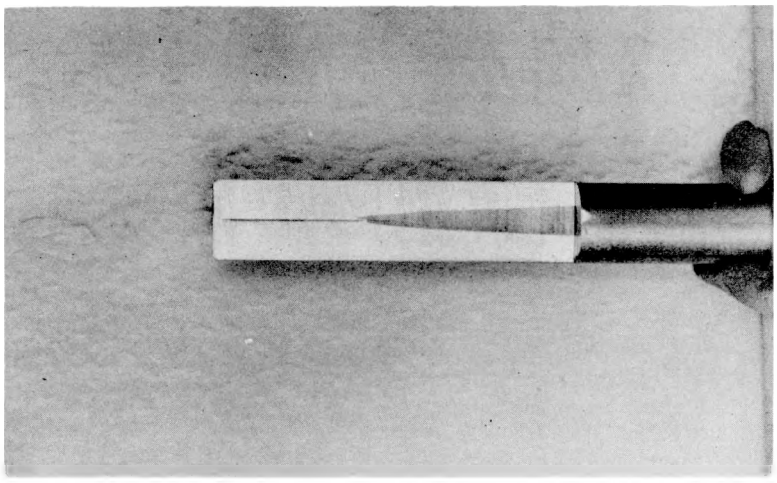


Fig. 23 - Distance from original uranium-Zircaloy-2 interface to layers composed of 10 a/o U and 10 a/o Zr in Zircaloy-clad U - 2 w/o Zr rods after heat treatments of various durations at temperatures shown.(1)



RF-5027

Fig. 24 - 7-mil diameter uranium thread in as-extruded Zircaloy rod after left end (above) was exposed to 650°F water for over 1000 hours. This corroded portion appears on the left and is slightly darker and broader than the uncorroded portion.

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