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WAPD - 127 - PART II
AEC RESEARCH AND
DEVELOPMENT REPORT

DEVELOPMENT AND PROPERTIES
OF URANIUM-BASE ALLOYS
CORROSION RESISTANT
IN HIGH TEMPERATURE WATER
PART II - ALLOYS WITH PROTECTIVE CLADDING

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Oak Ridge, Tennessee
September 24, 1957

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Westinghouse Electric Corporation
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Subject: DECLASSIFICATION OF WAED-127, PART II

Dear Mr. Simpson:

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CORROSION RESISTANT IN HIGH TEMPERATURE WATER

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PART II

Metallurgy and Ceramics
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DEVELOPMENT AND PROPERTIES OF URANIUM-BASE ALLOYS
CORROSION RESISTANT IN HIGH TEMPERATURE WATER

Part II - Alloys With Protective Cladding

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September 7, 1955

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I. Synopsis

Several gamma phase uranium-molybdenum (U-Mo) and uranium-niobium (U-Nb) alloys and one epsilon phase (U-Si) alloy which had been shown to have good corrosion resistance in high temperature water and steam when tested in the bare condition were selected for study of their corrosion behavior when clad with Zircaloy-2 by coextrusion. Simulated rod-shaped fuel elements from these extrusions, provided with welded Zircaloy-2 end caps and small size defects intentionally machined completely through cladding and part way through the core alloy, were used to investigate the corrosion resistance of the fuel alloy and the mechanism of failure as affected by the presence of the bonded cladding. Simulated fuel elements prepared from some 57 extrusions containing binary and ternary core alloys of various chemical compositions were corrosion tested in various conditions of fabrication and heat treatment. The results of the investigation are summarized briefly below.

Corrosion life tests were performed first on fuel element samples prepared from induction melted and cast alloys of the following nominal compositions: U-9, -10.5, -12, and -13.5 w/o Mo, U-10 w/o Nb, U-6 to 12 w/o Mo-0.5 to 3 w/o Nb, and U-3.8 w/o Si. No heat treatments were applied to the ingots or to the clad extrusions until later in the investigation. Sections of the extrusions were prepared as fuel element samples, defected with 0.040 in. diam holes and corrosion tested in 650°F degassed water, and, in some cases, in 680°F water and 750°F steam. Considerable variation in corrosion life was displayed by the different alloys in the 650°F water tests. For the U-9, -10.5, and -12 w/o Mo samples the variation in corrosion life was 76 to 199 days, 56 to 176 days, and 49 to 268 days, respectively. The U-13.5 w/o Mo alloy samples displayed less variation, failing in 273 to

to 342 days. The U-10 w/o Nb samples failed in 158 to 330 days. Of the ternary alloy samples tested the clad U-10.5 w/o Mo-1.5 w/o Nb alloy appeared most promising. Although only one sample of this alloy was tested at 650°F, it had a life in excess of 308 days. The U-3.8 w/o Silicon alloy, which showed excellent promise in the bare condition behaved very poorly in the clad condition. Fuel element samples of this alloy were subject to rapid corrosion attack at the core-clad interface and failed within 14 days. Failure times were correspondingly shorter for clad alloy samples tested at 680°F and 750°F and variation in failure times for any given alloy were also quite apparent.

Because of the relatively large variability in corrosion life displayed by the fuel element samples, and in particular those prepared with a U-12 w/o Mo core alloy whose excellent thermal and irradiation stability made it especially desirable as the fuel alloy for the Pressurized Water Reactor, an investigation was undertaken to determine the major factors responsible for variations in corrosion life.

Careful examination of failed sample elements indicated that three major types of failures can occur with clad and defected fuel elements:

1. Pimpling of the cladding at the site of the defect caused by a localized build-up of oxide at the base of the defect. This type of failure usually occurs at high corrosion temperatures (680°F water or 750°F steam) and is associated with the relatively high corrosion rates of the fuel at these temperatures. Corrosion failures of this type are usually associated with long corrosion lives.
2. Discontinuous cracking of the fuel in gamma phase core alloys with subsequent rapid corrosion of the fuel and rupture of the cladding.

This type of failure is associated with gradual release of nascent hydrogen during corrosion of the exposed fuel and absorption of a portion of the hydrogen by the core alloy. When the solubility of hydrogen is exceeded in the core, hydride platelets precipitate and corrode rapidly. The lower density of the corrosion product results in cracking and rapid disintegration of the fuel alloy and rupture of the cladding. Since the Zircaloy-2 cladding is a hydrogen getter, the amount of hydrogen absorbed by the core alloy is appreciably reduced (compared to the case of bare samples). In the absence of other adverse corrosion effects, therefore, failure by hydrogen absorption through 0.040 in. diameter cladding defects normally occurs only after very long exposure to 650°F water. However, if through poor fabrication procedures poor clad-core bonding is produced and hydrogen diffusion thereby impeded, rapid failure may occur, generally at a location remote from the intentional defect.

3. Formation of corrodible core-clad interdiffusion layers.

The formation of such layers during extrusion of clad U-Si rods is responsible for very rapid failure of defected fuel element samples since the entire surface area of the core alloy is rapidly exposed to the corrosive action of high temperature water and build-up of surface oxide ruptures the cladding. In the case of gamma phase alloys such corrodible diffusion layers are not normally formed during extrusion. They will form and lead to rapid failure, however, if the extrusion is subsequently subjected to a high temperature heat treatment.

Heat treatment after extrusion and its effect on the corrosion behavior of clad fuel element samples was investigated in some detail. It was previously stated that the first corrosion tests performed on defected

fuel element samples involved core alloys which were induction melted, cast and then extruded with Zircaloy-2 cladding. This fabrication procedure was not effective in homogenizing the core alloy and resulted in alloy segregation which takes the form of longitudinal stringers in extruded rods. The stringers were found to be highly corrodible, resulting in early failures of unclad samples by fibrous splitting. To eliminate alloy segregation a high temperature (900-1000°C) homogenization treatment was employed. In the case of bare extrusion samples this was very effective in improving corrosion resistance. When applied to clad extrusions, however, highly corrodible core-clad interdiffusion layers formed.

A study of the interdiffusion of core and cladding was undertaken at Westinghouse Atomic Power Division, Bettis Site, using coextruded rod samples and at Battelle Memorial Institute (BMI) under Subcontract 73-(14-383), on pressure-bonded flat samples. In both cases U-12 w/o Mo was used as the core alloy. It was found that core-clad interdiffusion layers containing 59-78 w/o U, 18-35 w/o Zr, and 9-12 w/o Mo formed during high temperature annealing and that these layers have poor corrosion resistance and are responsible for the bond-line attack observed during 650°F corrosion tests. Diffusion tests were also carried out on coextruded rods having a U-10 w/o Nb core. While it was found that bond-line attack also occurs in this case, the attack is less rapid than for the corresponding case of U-Mo clad alloys.

The effectiveness of various metallic barrier layers in eliminating core-clad interdiffusion and permitting high temperature homogenization treatments was investigated. Barrier layers of Ni, Fe, Cr, Mo, Ta, Pt, and U-10 w/o Nb were investigated by pressure bonding at BMI using a U-12 w/o Mo core alloy while Mo, Nb, Pt, Pd, U-15 w/o Mo-5 w/o Pt, and U-10 w/o Nb

barriers were investigated at the Bettis Plant by coextrusion techniques using a U-10.5 w/o Mo core alloy. Included with the extruded material was a rod prepared with a Nb barrier and a U-10 w/o Nb core alloy. The pressure bonded samples all failed by severe bond-line attack within 7 days. Relatively thick diffusion layers were formed at the clad-barrier and barrier-core interfaces. None of the coextruded samples containing a U-10.5 w/o Mo core was entirely satisfactory although some promise was indicated for Mo and Nb barriers. The Nb barrier with the U-10 w/o Nb core alloy successfully extended the life of the fuel elements in both the as-extruded and heat-treated condition. Defected fuel element samples prepared in this way have withstood satisfactorily 210 days exposure to 650°F water.

The feasibility of reducing alloy segregation without resorting to a high temperature homogenization treatment after extrusion was investigated simultaneously with the barrier layer studies. It was found that the cast alloy ingot could be very effectively homogenized before extrusion. Corrosion rates in 650°F water of bare samples of U-12 w/o Mo which were homogenized either before or after extrusion turned out to be the same, about 0.2 mg/cm²/hr. Longitudinal splitting, characteristic of samples containing stringer type alloy segregation, was largely eliminated. In the case of clad extrusions it was found that the presence of stringer type segregation does not have as marked an effect on corrosion life of defected elements as is the case for unclad material. This may be due to the decreased probability that the introduced defect will penetrate to an area containing stringers. At any rate any variability in corrosion life that may result from the presence of stringers

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in clad fuel elements would be materially reduced by prior ingot homogenization. Through prehomogenization of the ingot, therefore, the need for heat treatment after extrusion is largely eliminated. Core-clad interdiffusion which occurs during the very short extrusion cycle (about 30 seconds) results in extremely thin diffusion layers. These are not subject to the rapid corrosion attack observed for relatively thick diffusion layers formed when clad extrusions are homogenized.

Another factor considered in the observed variability of corrosion life involved reducing alloy segregation in the induction melted and cast alloy ingot by using the ingot as a consumable electrode and remelting it in an arc furnace provided with a water-cooled copper crucible. This duplex melting process not only reduced alloy segregation but also produced completely sound ingots free of center porosity which was often observed in the induction melted and cast product. Defected fuel element samples prepared from clad extrusions of duplex melted U-10.5 and -12 w/o Mo, U-10 w/o Nb-1 w/o Pt, U-8 w/o Mo-1 w/o Pt, and U-12 w/o Mo-0.5 w/o Pt, with or without the benefit of an homogenizing heat treatment before extrusion, have shown remarkably long life in 650°F water. Fuel elements prepared in this way have thus far withstood 182 days of test for the first two core alloys and 210 days of test for the latter three core alloys with no failures recorded. By combining duplex melting with homogenization before extrusion a good quality core alloy is consistently achieved. Coextrusion with Zircaloy-2 cladding then results in a very thin core-clad interdiffusion layer which is not subject to rapid corrosion. The necessity for using barrier materials interposed between cladding and gamma-phase core alloys no longer exists. In fact, barrier layers (with the exception of Nb applied

between U-10 w/o Nb and the cladding) have not been successful in permitting homogenization after extrusion.

The effect of cold drawing, after extrusion, on the corrosion behavior of fuel element samples was investigated because of its possible use as a production fabrication step to obtain final size and dimensional accuracy. While unclad samples obtained from cold drawn (40 to 55% area reduction) extrusions of U-12 w/o Mo show little, if any, deterioration of corrosion resistance, clad defected fuel element samples show a marked reduction in corrosion life. Fuel element samples which received over 40% cold reduction failed within 14 days in 650°F by rapid attack at the core-clad interface. Lower amounts of cold work (17 and 30%) are not as disastrous, the earliest failures being recorded in 168 days. However, even a small amount of cold work is to be avoided since it reduces the thermal stability of the core alloy resulting in relatively rapid transformation of the corrosion-resistant metastable gamma phase. It appears that the deleterious effects of cold work, however, may be avoided by a low temperature, short time anneal (5 to 10 minutes at 700°C) without causing excessive growth and rapid corrosion of core-clad interdiffusion layers. Samples cold worked 53% and heat treated in this manner have survived over 112 days in 650°F water. Additional data, however, would be required to confirm these results.

The effects of several other variables on the corrosion behavior of clad extrusions of U-12 w/o Mo were also investigated. These included the size of cladding defects, cladding thickness and design of welded end plugs used on fuel element samples. Of these, only the size of cladding defects was found to be related to corrosion life in 650°F water.

As might be expected it was found that the corrosion life decreases as the area of fuel exposed through the defect increases. When relatively large areas of fuel are exposed, corrosion of the gamma-phase core alloys takes place over a larger area, correspondingly more hydrogen is absorbed by the fuel element sample, and failure occurs earlier. The effectiveness of the cladding as a hydrogen getter, reducing the amount of corrosion hydrogen absorbed by the core alloy, would be expected to be reduced in proportion to the increase in defect size. It was noted, however, that even large areas of exposed fuel were protected by the presence of the zirconium clad. Thus completely exposed cross-sections of fuel element samples survive much longer than do bare samples. This protection may be ascribed to the relatively high rate of diffusion of hydrogen in gamma-phase uranium alloys and to the hydrogen gettering of the Zircaloy cladding. To eliminate defect size as a variable in evaluating corrosion life of various fuel element samples, it was standardized at 0.040 in. diameter as previously stated.

II. Introduction

This report is the second in a series on the "Development and Properties of Uranium-Base Alloys Corrosion Resistant in High Temperature Water". Part I of this series (WAPD-127) was entitled "Alloys Without Protective Cladding".¹ It was concerned with the investigation of the corrosion resistance of various uranium-base alloys in the unclad condition. From this work several alloys in the U-Mo and U-Nb systems, including alloys containing small ternary additions of platinum, were found to have very promising corrosion resistance in hot water or steam. The corrosion

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resistance of these alloys, however, is not sufficiently high to permit them to be used as reactor fuels operating in these media without a suitable protective cladding. The cladding is needed to protect the fuel alloy from the corrosive action of high temperature water, to prevent contamination of the primary reactor loop from radioactive corrosion products and recoil fission fragments from the fuel and to hinder irradiation induced dimensional changes in the fuel alloy.

Zircaloy-2, a zirconium alloy containing 1.5 w/o Sn, 0.12 w/o Fe, 0.10 w/o Cr, and 0.05 w/o Ni, has been used as the protective cladding material in pressurized water reactors because of its excellent corrosion resistance in high temperature water and because of its low neutron absorption cross section. In continuation of the development of improved fuel elements for pressurized water reactors, therefore, it is necessary to consider not only the corrosion resistance of unclad fuel alloys, but also the behavior of these alloys when prepared as clad fuel elements, simulating the final fuel elements as they would be used in the reactor. Of particular concern is the integrity of the cladding. Since any cladding defects, originating during fabrication or developing during reactor operation, will expose the underlying fuel to corrosion attack by water, it is important that the fuel be capable of resisting such attack for prolonged periods.

The corrosion resistance of uranium-base alloys and mechanism of failure in high temperature water is influenced strongly by the presence of the cladding. This was shown by corrosion testing of simulated rod-shaped fuel elements in which artificial defects were intentionally introduced in the cladding. This report (Part II in the series) describes the corrosion behavior of such rod-shaped elements fabricated by hot

extrusion and employing as cores the various uranium-base alloys displaying the most promising corrosion resistance on the basis of previously reported results on bare samples. Also included in this report is a discussion of the types of corrosion failures encountered in clad fuel elements and the various investigations undertaken to improve corrosion resistance. Some discussion is also presented of the mechanism of corrosion and ultimate failure of the elements as influenced by the presence of the cladding. The mechanism of corrosion as applied particularly to unclad uranium-base alloys, will be treated in detail in a separate report, Part III, entitled "Mechanism of Corrosion". A fourth report, Part IV, entitled "Irradiation Induced Effects" will complete the series and describe the behavior of the most promising uranium-base alloys when subjected to in-pile irradiations.

This report covers corrosion life data on simulated fuel element samples prepared from 57 clad extrusions prepared with U-Mo and U-Nb core alloys of various compositions. Included in these extrusions are a few prepared with the epsilon-phase U-3.8 w/o Si alloy. The latter represent very early and preliminary work on the epsilon phase alloy. They are included for the sake of completeness. A very intensive program on alloys of this type is now under way and will be reported upon at a later date. Of the 57 extrusions discussed in this report 34 were prepared using core alloys which were induction melted and 23 using core alloys which were induction melted followed by consumably remelting in an arc furnace. The latter duplex melted ingots were found to be more desirable from the standpoint of greater homogeneity of alloying elements and lack of center porosity. A considerable amount of effort was expended in evaluation of extrusions in various conditions of fabrication and heat treatment and

many of the factors influencing corrosion life of defected rod elements are now understood.

III. Extrusion Cladding Process and Sample Preparation

The extrusions used in this work were fabricated by the FWR Fuel Element Subdivision at the Bettis Plant. Pertinent information concerning the cladding process and subsequent sample preparation is described below. Complete information on melting, casting and fabrication procedures is contained in references 2, 3, and 4.

The core alloys were originally prepared by vacuum induction melting in BeO, MgO or graphite crucibles provided with a ZrO_2 wash. These were chill cast in vacuum into graphite molds 1.50 in. diam. with a ZrO_2 wash, or in water cooled copper molds. The castings were machined to fit snugly into Zircaloy-2 cup-shaped containers 1.200 in. inside diameter by 3.0 in. long. A Zircaloy-2 plug was then welded onto the open end of the container in an helium-filled dry box. These assemblies were heated in salt at 1040°C for 15 minutes for most U-Mo or U-Nb alloys and immediately extruded through a 0.314 in. diameter die. In the case of U-Si core alloy extrusion was carried out at 920°C or less to prevent transformation to phases of low corrosion resistance. A few assemblies were extruded through 0.375 in., 0.500 in., or 0.75 in. diameter dies. The core diameters, determined by X-ray radiography after extrusion, were quite uniform and for most extrusions varied between 0.250 in. and 0.260 in. The nominal outside diameter of these extrusions was 0.314 in. and the clad thickness was 0.030 in. The reduction of cross sectional area of the uranium alloy core was 96%.

For the duplex melted U-Mo and U-Nb core alloys the 1.50 in. diameter induction melted and chill cast ingots were consumably arc-melted to 2.3125 in. diameter ingots. The induction melted ingots formed the consumable electrode in an arc furnace having a water cooled copper crucible. The 2.3125 in. diameter ingots were machined to a final diameter of 1.892 in. and sectioned into billets 3.25 in. long. The billets were assembled into Zircaloy-2 containers, end-plugged as described above, and placed in welded steel jackets. After heating for 15 minutes in a salt bath at 875°C the assemblies were extruded through a 0.50 in. or 0.437 in. diameter die. The reduction of cross-sectional area of the core alloy for the larger diameter was about 96% as calculated from an average core diameter of 0.370 in.

It was recently found that it is desirable to homogenize the cast structure of the core alloy at 900-1000°C prior to extrusion. Two of the U-12 w/o Mo alloy extrusions were prepared from duplex melted ingots heat treated in this manner. Attention will be called to this when discussing these extrusions in the body of the report. Also, one-half of each extrusion prepared from duplex melted ingots was cold drawn to study the effects of this variable on corrosion behavior. The amount of cold drawing varied in the range of 15% to 56% reduction in area for different extrusions. The amount of cold drawing for a particular extrusion, therefore, will be indicated in the body of the report.

It was often found desirable to corrosion test clad rod samples with bare ends (fuel exposed at each end). For the most part, however, it was desired to simulate as closely as possible the actual conditions that prevail in a reactor using rod-shaped fuel elements. Thus, 3 in. lengths

of fabricated clad rod were machined at each end to remove the core alloy to a depth of 0.25 in. Zircaloy-2 plugs were fitted into these cavities and welded to produce leak-tight end closures. Artificial cladding defects were then introduced by drilling holes completely through the cladding and part way through the fuel alloy. In the case of heat treated rod elements, the defects were introduced after heat treatment. Except in special cases where the effect of defect size was of special interest, the defect diameter was arbitrarily set at 0.040 in.

All corrosion tests were carried out in static degassed water at 650 or 680°F or in 750°F steam using stainless steel type autoclaves.

IV. Types of Corrosion Failure as Affected by Cladding

As described in Part I of this series of reports, bare samples of gamma-phase alloys fail in 650°F water in times varying from 14 to 100 days, averaging about 14-28 days. Bare samples of the epsilonized U_3Si alloy corrode by continuous surface oxidation. When these same alloys are clad and tested as described in Section III above, failure may be delayed by as much as 10 to 20 times as long as the times noted for the bare samples, although the corrosion rate based upon the exposed area appears unaffected. Alternatively, failure times may be less than those encountered in case of bare samples.

Corrosion life of clad samples was terminated by extensive failure. Such failures fall generally into three categories: failure at the location of the defect which occurs generally only at high temperatures (750°F) or long times (over 300 days); failure by discontinuous cracking occurring at somewhat shorter times; failure due to unbonding which may

occur in very short times and is characteristic of mistreated samples and the U_3Si alloys. These failures are discussed in greater detail below.

A. Pimpling at Hole Defects

In Fig. 1(A) are shown three simulated fuel elements tested in 750°F steam (1500 psi) for 58 days. All are from the same extrusion (No. 8 CI) containing a 10.5 w/o Mo core alloy. The rod was centerless ground after extrusion and three 0.040 in. diameter holes (one in the middle of the rod diametrically opposite the two shown) were drilled about 0.015 in. into the core alloy.

During the first 44 days of testing the elements showed no evidence of corrosion attack. Pimples then grew at the holes until complete rupture of the cladding occurred during the 58-65 day period of testing. In Fig. 1(B), polished cross sections through two holes of element No. 27 indicate that the pimples result from a localized build-up of oxide. Fig. 1(C) shows the failure of the remaining two elements during the 58-65 day corrosion test period. The Zircaloy cladding that remains of No. 26 is shown exactly as it was removed from the autoclave. Failure apparently took place by periodic cracking of the core alloy causing a continuous stepwise peeling back of the cladding which is evidenced by the creases on the outside cladding surface apparent in the bottom illustration.

This type of failure is not generally observed when testing in 650°F water. It appears to occur at high temperatures where the rate of corrosion of the fuel alloy is relatively rapid.

B. Discontinuous Cracking Failure

The typical manner in which bare gamma phase alloys fail is by cracking into pieces during a comparatively short period of testing compared to the total accumulated test time prior to failure. This behavior has been covered extensively in Part I of this report. For the bare alloys of best corrosion resistance the cracking failure is preceded by a long period of uniform weight loss and formation of a shiny adherent scale. The time for cracking failure can vary considerably even for samples cut from the same alloy so that it is difficult to obtain an accurate value for corrosion life of bare samples. Sample geometry and ratio of area to volume, among other things, appear to influence the discontinuous cracking. Again, in the case of clad samples, a long period during which the sample is unaffected is noted, followed by a period of rapid failure, the failure being attended by local cracking of the core alloy, generally at locations remote from the defect.

In seeking causes for cracking, residual stress, stress corrosion, and phase transformations have been considered. However, as-cast samples as well as gamma-quenched and low-temperature annealed samples are all prone to corrosion cracking. There is now good evidence that reaction of hydrogen with the gamma-phase uranium alloys is the underlying cause of discontinuous cracking. A plate-like phase has been observed in most samples that have cracked and has been identified by hydrogen analysis of corroded samples as resulting from hydrogen absorption during the corrosion test. Although this topic will be examined in greater detail in Part III, "Mechanism of Corrosion Failure", the mechanism of the hydrogen reaction as it pertains to failure of clad rods will be presented here.

During corrosion, gamma-phase uranium alloys react with the oxygen of the water at the sample surface. Some of the nascent hydrogen thus produced does not recombine to form gas but instead diffuses into the metal. When the solid solubility of hydrogen in the uranium alloy is exceeded, precipitation occurs in the form of platelets which are observable microscopically. The diffusion rate of the hydrogen is presumed to be extremely rapid since the platelets appear uniformly dispersed in the corrosion samples examined. Hydrogen analysis indicates an increase from about 1 ppm before testing to about 25 ppm when precipitation is first observed. Hydrogen content increases continuously thereafter as still more hydride precipitates. Hardness of the alloy has also increased. At this point the alloys are believed to be prone to cracking since it has been observed that the samples are greatly embrittled by hydride precipitation. Oxidation of exposed surfaces when cracking occurs with a consequent volume increase may then give rise to rapid disintegration of samples. In Fig. 2(A) is shown the unetched microstructure of a clad U-Mo alloy rod that failed as a result of cracking. The oxide retained at the tip of a large crack (upper left corner) is seen to be preceded by a branching of smaller cracks (probably the oxidation of hydride plates governs to some extent the direction of these cracks). Stress arising from the volume increase due to such localized oxidation could result in propagation of another long range crack which would then undergo the same localized oxidation. By this means eventual disintegration of the sample would result.

The important factor, therefore, in the cracking phenomenon is the ability to build up a sufficient hydrogen concentration in the uranium alloy. The rate of hydrogen pickup is a function of the total amount of

corrosion (i.e., the nascent hydrogen available) which in turn is proportional to the amount of surface exposed to the water and also a function of the fraction of corrosion hydrogen which remains in the core alloy. It will be shown in the next section that in the case of elements in which the core and cladding are not bonded, hydride precipitation and cracking of the core alloy occur rapidly because of the large corroding surface area and because the hydrogen cannot diffuse into the cladding. On the other hand, well bonded elements which are not subject to bond-line corrosion have long corrosion lives and an absence of hydride precipitation. In Fig. 2(B) a cross section is shown of a hole defect in a 12 w/o Mo alloy sample (No. 206) tested 252 days in 650°F water. Note in Fig. 2(b) the thick oxide scale overlaying the uranium alloy. The sample was carefully polished in order to preserve the oxide scale. High magnification examination indicates a complete absence of hydride precipitation in the uranium alloy of this sample and also for nine other defected samples tested for long times without failure.

A cross section of one of the holes of an as-extruded U-10 w/o Nb alloy which showed no outward evidence of corrosive attack after 330 days in 650°F water is shown in Fig. 3(A). At high magnification a eutectoid phase transformation at grain boundaries and a dendritic network is apparent in the core alloy as shown in Fig. 3(B). By microexamination of the corrosion around the defect it was seen that the alpha phase--dark phase in Fig. 3(B)--is selectively attacked, however, the long life experienced by this element can be attributed to the discontinuous nature of the alpha phase in a matrix of corrosion resistant gamma phase.

Thus it is postulated that the following occurrences are responsible for the long corrosion life of certain samples:

(1) No rapid corrosive attack at the core-clad interface occurs, thus limiting the surface area exposed to water. The rate of formation of nascent hydrogen relative to the total volume of core alloy is then low for alloys with low corrosion rates.

(2) The rate at which the available hydrogen diffuses into the core alloy and into the cladding is believed to be rapid, and the volume of metal into which it diffuses is large, so that a hydrogen build-up sufficient to cause precipitation, hardening, and hence embrittlement is not reached. Furthermore, since the Zircaloy cladding has a greater solubility for hydrogen than the uranium alloy, it will have a tendency continually to remove hydrogen from the core provided any damage to the interface does not act as a barrier to such transfer. The relative effectiveness of the Zircaloy cladding as a getter for hydrogen versus the size of defect in limiting failure cannot be assessed at present. Certainly, if corrosion were directly a function of the ratio of exposed area to total volume, the corrosion life of rods with 40 mil defects should be extended over that of bare samples much more than the 10 to 25 times actually observed. As will be discussed in Part III of this series of reports, insufficient data on solubility, diffusion rates, etc., of hydrogen in gamma-phase alloys are available to assess quantitatively the effect of cladding.

(3) Alpha uranium that may be present in the core alloy as a result of transformation of the gamma phase will readily react with hydrogen available from the nearby corroding surface. Such alpha uranium regions may act as loci for entrapment of hydrogen and may even hinder corrosion failures if the alpha regions are discontinuous.

C. Attack at Core-Clad Interface

When coextruded rods are heat treated at a high temperature diffusion layers are formed between the core and cladding. Such layers contain composition ranges which are less corrosion resistant than either the core alloy or cladding. The appearance of two elements which have been sectioned longitudinally after corrosion testing are illustrated in Fig. 4. Corrosion rapidly proceeds along the interface and completely envelops the core alloy in a sheath of corrosion product. The reaction proceeds most rapidly at the corners of the core alloy so that swelling and rupture of the cladding invariably occurs at the base of the end plugs. No pimpling occurs at the drilled holes. In Fig. 5(A) the corrosive attack for a U-10 w/o Nb sample (No. 327) heat treated at 800°C for 24 hr is seen to be confined to the interface. A sufficient amount of the nascent hydrogen produced by this reaction, which completely separated the core and cladding, diffused into the core alloy and produced a hydride precipitate visible in the high magnification view of Fig. 5(B). In the photograph of this same specimen, Fig. 5(C), the interface attack and a few small cracks can be seen on the cross section piece. The typical swelling and rupture of the cladding at the base of one end plug is also apparent. While this element failed during 112-126 days of testing in 650°F water, four other elements of the same material in the as-extruded condition (without a subsequent high temperature heat treatment) showed no evidence of corrosion attack when tested for periods ranging from 196 to 252 days. All clad ϵ -U₃Si alloys tested with 40 mil defects in 650°F water fail in this manner.

It is therefore believed that depending on fabrication history and post-fabrication treatment, Zircaloy-clad "corrosion-resistant" uranium alloys will fail by Type A failures at the defects after long periods of exposure if they are properly fabricated; if mistreated, samples fail with Type C failures at relatively short times; intermediate corrosion lives and type B failures are noted in samples of intermediate quality.

V. Interdiffusion of Core and Cladding

Heat treatment of the extruded core alloy is desirable to homogenize the structure and realize complete transformation to the corrosion-resistant gamma phase. This may be easily done on unclad extrusions. In the case of coextruded elements, however, it was seen that the diffusion layers formed at the core-clad interface contribute to early corrosion failure. Consequently, the growth of diffusion layers was studied as a function of time and temperature for several binary core alloy and cladding couples prepared by coextrusion. This work was later expanded to include extrusions with various metallic barrier layers between cladding and core. A similar program was initiated at Battelle Memorial Institute under subcontract 73-(14-383) to Westinghouse Atomic Power Division, making use of pressure bonding techniques to form the diffusion couples. The results of these investigations are discussed below.

A. Diffusion of Coextruded Binary Couples

With the exception of uranium metal clad with crystal bar zirconium the binary diffusion couples listed below were prepared as coextruded rods. The uranium-crystal bar zirconium sample was prepared by rapidly induction melting and solidifying uranium metal in a crucible machined from zirconium.

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1. Uranium : : Crystal Bar Zirconium
2. U-12 w/o Mo : Zircaloy-2
3. U-10 w/o Nb : Zircaloy-2
4. U-3.8w/o Si : Zircaloy-2

Sections of the rods served as diffusion couples. These couples were annealed in vacuo at 700°C, 800°C, and 900°C for times ranging from 1 to 72 hours. The results are shown in Fig. 6 where the total metallographically visible diffusion layer thickness is plotted against the square root of annealing time in hours. The straight line relationship indicates parabolic growth of the layers with respect to time. It should be noted that these curves represent the total thickness of two layers, one in the Zircaloy and one in the uranium alloy. It was found that the diffusion zone in the Zircaloy or Zirconium was about twice as wide as the corresponding zone in the uranium or uranium alloy. This condition is shown in Fig. 7 for typical diffusion zones formed by annealing these couples for 24 hr at 800°C. Except for the U-Si couple, note that the visible penetration forming the interface in the zirconium or Zircaloy is 1-1/2 to 3 times greater than the penetration into the uranium or uranium alloy where no sharp interface is apparent. The diffusion zone into the Zircaloy represents the composition range of uranium solubility corresponding to that which stabilizes the gamma phase of zirconium; the diffusion zone of zirconium into the gamma-phase U-Mo and U-Nb alloys shows a recrystallized, fine-grained microstructure with precipitates of a second phase. The similarity of the layer thickness in the Zircaloy for the various couples would indicate that the rate of migration of uranium and zirconium atoms is only slightly influenced by the presence of molybdenum or niobium atoms. The slow growth of the diffusion layer for

the U-Si alloy has been recently (WAPD-TN-523)⁵ shown to be caused by the formation of layers of a zirconium silicide and alpha uranium--Fig. 7(d).

It is possible from the data in Fig. 6 to obtain an activation energy for the rate of diffusion layer growth in the Zircaloy-2 : U-12 w/o Mo couple. The relationship between the diffusion coefficient, thickness, and time is given by the equation

$$D = K \frac{x^2}{t}$$

where D is the diffusion coefficient, x is the thickness, t is the time, and K is a proportionality constant. The activation energy is obtained by plotting $\ln(\frac{x^2}{t})$, the ln of the slope of the growth curves, against the reciprocal of the absolute temperature. This has been done in Fig. 8 and yields an activation energy, Q, of 55,000 calories per mol.

A few as-extruded elements have given an indication of failing because of interface corrosion. Since the only solid state interdiffusion of clad and core would occur during the approximate 30 seconds for extrusion and cooling from 1600°F, the diffusion layer formed would be expected to be negligible. Of about 15 extrusions examined the diffusion layer of none varied appreciably in thickness (about 10^{-4} in.) and appearance from the three shown in Fig. 9. In spite of what appears to be the typical two-layer diffusion zone, none of the long time corrosion tested elements of these alloys showed penetration along the bond line at the drilled holes in the cladding. It is believed that layers of the thickness shown are unaffected in corrosion. The failures similar to those found in interface corrosion are believed to result from unbonding during fabrication.

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B. Diffusion Couples Prepared by Pressure Bonding

The nature of the bond interface between Zircaloy-2 cladding and U-12 w/o Mo core alloy was studied by Battelle Memorial Institute (BMI) and involved diffusion couples prepared by pressure bonding of components in vacuum at elevated temperatures using the conventional picture-frame technique. A detailed BMI report⁶ covering this work was recently issued so that only a brief summary of important results will be indicated here.

Several diffusion layers of various compositions are formed when U-12 w/o Mo coextruded with Zircaloy-2 is annealed at 900°C. These layers, shown in Fig. 10, were confirmed in pressure-bonded couples prepared by BMI. Corrosion tests in 650°F water of couples defected with 0.040 in. diameter holes indicated that failure would occur within 72 hours due to interface attack. A few samples, bonded to produce diffusion layers as thin as possible, lasted somewhat longer. The life of these samples, however, was considerably shorter when compared to coextruded elements since the diffusion layer thickness is invariably greater in pressure-bonded samples.

Pressure-bonded samples heat treated to produce thick diffusion layers (such as those shown in Fig. 10) were sectioned and corrosion tested in 650°F water for short periods in order to detect the location of initial attack. Results indicated that attack occurred in the white area (layers 4 and 5 of Fig. 10), attack being visible within 1/2 hour. Within 2 hours of test these layers are essentially completely corroded, leaving a 5 mil void.

The chemical composition of the various layers, indicated in Fig. 10, were determined by careful machining followed by spectrographic, chemical and X-ray fluorescent analyses. The composition of each layer

is listed below:

Layer No. (Refer to Fig.16)	Chemical Analysis, w/o			
	Mo	Sn	U	Zr
1	0.15	1.45	2.1	94.0
2	3.1	1.3	18.6	84.0
3	7.4	0.65	45.8	43.0
4*	9.2	0.5	59.1	35.0
5*	12.3	0.5	78.0	18.0
6	Identified by X-ray diffraction as ZrMo ₂ compound			
7	12.8	0.5	85.3	1.5
8	12.3	-	89.0	-

* Layers which were shown to corrode rapidly.

While the compositions of the various layers may not be accurate because of difficulties in isolating them for machining purposes, it was considered desirable to prepare melts of the alloys so that their corrosion properties could be studied individually. It was found that alloys corresponding to layers 4 and 5, which had a retained gamma structure, were rapidly attacked within 24 hours in 650°F water, failing in both the annealed and gamma-quenched conditions. The alloy corresponding to layer 5 showed evidence of attack within 1/2 hour and disintegrated within 24 hours. The alloy corresponding to layer 4 showed no attack in 2 hours but was cracked and warped within 24 hours. Similar 24 hour results were obtained when these alloys were coupled with others having compositions corresponding to adjacent layers. Alloys corresponding to layers 1, 2, 3 and 6 were found to have good corrosion resistance.

It was apparent from the above results that the diffusion layers containing 9-12 w/o Mo, 59-78 w/o U, and 18-35 w/o Zr are poor in corrosion resistance and are responsible for the bond-line attack in coextruded U-12 w/o Mo rods which are subjected to a high temperature heat treatment after extrusion. One possible way of avoiding this type of attack and still permitting high temperature heat treatment after extrusion

is to interpose a suitable metallic barrier layer between core and cladding. This possibility was investigated and is discussed below.

C. Interface Metal Barrier Layers Prepared by Pressure Bonding

Pressure-bonded samples, containing barrier layers, were investigated by BMI⁷. These barriers included chromium, iron, and nickel electroplated on the core alloy, and foils of molybdenum (0.005 in.), niobium (0.002 in.), tantalum (0.002 in.), and an alloy of U-10 w/o Nb (0.004 in.). None of these were successful in prolonging the life of defected samples. The life in 650°F water was about 7 days for the chromium and tantalum containing samples and less for the others. Since very thin interdiffusion layers are obtained in coextruded rods, these results do not preclude the possibility of satisfactorily interposing suitable barriers by the extrusion process. Information on such rods has been obtained using various materials as barriers and is presented in the following section.

D. Interface Metal Barrier Layers Prepared by Coextrusion

Since interdiffusion of core and clad produced corrodible bond layers upon heat treatment after extrusion, molybdenum and tantalum were investigated as barrier layers. This was first done using induction-cast U-12 w/o Mo as the core alloy. Later this work was expanded to include molybdenum and several other barrier layer materials. The latter extrusions involved duplex melted (induction cast followed by consumably arc remelted) ingots of U-10.5 w/o Mo; they will be treated separately in Section IX.

For the molybdenum and tantalum barriers, 13 extrusions were prepared. The barrier material was interposed between the U-12 w/o Mo induction-cast ingots and Zircaloy-2 jackets as a foil and the composite

extruded directly to 0.31 in. outside diameter. The reduction ratio was 4 to 1 for the initial and final diameters so that a 10 mil thick foil, used for most extrusions, gave a final barrier thickness of 2 to 3 mils. The final Zircaloy-2 thickness was a nominal 30 mils. (Complete details concerning the manufacture of these rods is contained in WAPD-FE-231.)⁸ Of the 13 extrusions the following three were selected for diffusion and corrosion studies:

<u>Ext. No.</u>	<u>Barrier Metal</u>	<u>Approx. Thickness</u>
11W1-4	Mo	2 mils
11W1-10	Mo	0.3 mils
11W1-6	Ta	2 mils

In order for the principle of a barrier layer to be effective, it should be thick enough to prevent appreciable diffusion of uranium or zirconium atoms through it during the annealing time necessary to homogenize the uranium core alloy. Consequently, diffusion layer growth was studied as a function of time and temperature for the 0.002 in. barrier layer materials. The results are shown in Fig. 11 where diffusion layer thickness is plotted against the square root of the annealing time at 900°C in hours. Typical microstructures are shown in Fig. 12 showing the diffusion zone after 24 hours at 900°C for Mo and Ta barrier layer samples, respectively. A gap existed in the Ta barrier. Presumably the diffusion layer in the Zircaloy at this gap is representative of diffusion of uranium atoms while that opposite the Ta metal is representative of diffusion of Ta atoms. The diffusion layer thicknesses presented in Fig. 11 are therefore proportional to the relative rates of diffusion of U, Mo, and Ta, respectively, into Zircaloy-2. The actual diffusion rates must, of course, be corrected for the relative solubilities.

Short sections of the extruded rods containing barrier layers of Mo and Ta that were annealed at 900°C for various lengths of time to produce diffusion layers were corrosion tested at 650°F with the ends exposed to the water. The weight loss as a function of diffusion layer thickness is plotted in Fig. 13. The corrosion rates include weight loss of the alloy, the negligible corrosion of the cladding, and the rapid corrosion of the diffusion layer. Since the corrosion product of the diffusion layer sometimes washes out and sometimes remains as a hard packed deposit, the total weight change of the samples may be misleading. Furthermore, the corrosion rates are based on the original uranium alloy area exposed to water. In spite of these limitations it is evident that a Mo barrier layer decreases the bond line corrosion in annealed 12 w/o Mo alloys while Ta does not. The low rate of weight loss of the 10 w/o Nb alloys and absence of pronounced corrosion at the core-clad bond-line is revealing since annealed simulated fuel elements of the same material with holes drilled through the cladding also showed longer corrosion life and less severe bond-line attack than U-Mo elements. These results are presented in Section VI.

Standard simulated fuel element samples made from the three barrier layer extrusions were tested in 750°F steam after annealing 24 hr at 900°C. Some swelling occurred after the first 7-day test period and complete rupture of the cladding occurred after the second 7-day test period. The Mo barrier samples tested in 650°F water showed a single longitudinal split in the cladding after the 42-56 day test period, while the Ta barrier sample showed similar splitting under these conditions after the 56-70 day test period. It was found on cross sectioning the various samples that corrosion had proceeded along the uranium alloy immediately adjacent to the barrier as shown in Fig. 14 for the steam tested 0.3 mil Mo barrier sample and the 2 mil

Ta barrier sample. Corrosion in such a region was surprising because no corrodible phases or compounds would be expected to form as a result of annealing at 900°C.

Since some deleterious contamination or gaseous reaction at the uranium alloy surface just prior to extrusion was suspected, the following melting technique was tried in an attempt to produce a better condition at this particular interface. Crucibles with about 1.1 in. ID were machined from arc-melted molybdenum and from sintered molybdenum metal. The U-12W/o Mo alloys were then vacuum melted directly in these crucibles and directionally solidified by slowly raising the induction coil. When the molybdenum was machined from these ingots to a thickness of about 0.045 in., they were placed inside Zircaloy containers and extruded at 1050°C to 0.31 in. rod. Only one extrusion made from arc-melted molybdenum was satisfactory for further work. The barrier layer of the finished rod was about 0.010 in. thick, but on cross sectional examination had several fine hair-line cracks running axially which did not, however, extend into either the core or the cladding.

Corrosion data for simulated fuel elements from the extrusion with the molybdenum barrier and with the standard 0.040 in. diameter hole in the cladding at the middle of the rod are presented in Fig. 15. The as-extruded material was badly cored because of the slow solidification so that the poor behavior of these samples are believed to be the result of rapid corrosion of the core alloy. Of the three samples annealed at 900°C for 24 hours, one appeared to have had a defective barrier since bond-line corrosion and swelling and rupture of the cladding occurred at the base of the end plugs. The other two showed no dimensional change after 126 days of testing in 650°F water. A cross section at the hole of No. 128 is shown in Fig. 16. Note the equiaxed

grain structure of the gamma phase uranium alloy and the absence of hydride platelets. Note too that no appreciable corrosion of the diffusion zone between clad and barrier or barrier and core occurred as a result of the heat treatment.

From these data, it appears that core-clad interdiffusion and the resulting formation of corrodible layers severely limit post-extrusion heat treatment. While barrier layers may limit such damage, fabrication difficulties attending use of additional components prevent full exploitation of any advantages.

VI. Corrosion Life Data for Coextruded Rod Elements Prepared With Various Induction-Cast Core Alloys

While it was recognized that various types of failures could occur during corrosion testing of clad and defected rod elements in 650°F water, early corrosion life data indicated that rods prepared by direct bonding of the induction-cast core alloy with Zircaloy-2 cladding were very promising. Accordingly, several extrusions were prepared with induction-cast core alloys involving U-9, -10.5, -12 and 13.5 w/o Mo, U-10 w/o Nb, U-Mo-Nb ternaries and U-3.8 w/o Si. These were extruded directly with Zircaloy-2 cladding to 0.31 in. outside diameter and tested in 650 and 680°F water or 750°F steam. The purpose of these tests was to establish the effect of core composition on corrosion life and the effects of test temperature on variability of the more promising core alloys. Occasionally samples have been tested which remained over 300 days in 650°F water. Fabrication conditions necessary to produce such long-lived samples have not been isolated. Therefore in the following only such experiments are reported in which fabrication techniques were constant but not necessarily optimum.

All of the rod elements tested were defected by drilling a single 0.040 in. diameter hole through the clad and partially through the core alloy. The rods were examined visually after each 7 or 14 day test period for dimensional changes (bulging), or splitting of the cladding. It was found that most of the elements were dimensionally unchanged during testing until severe rupturing of the cladding occurred during a particular 7 or 14 day test period. This failure was indicated by a black block on the bar graphs referred to for the individual core alloys involved.

A. U-9 w/o Mo Core Alloy

Two extrusions were fabricated at about 980°C from a single ingot (Y-60) melted in an MgO crucible. The ingot was cast at 1450°C and analyzed 8.8 w/o Mo, 0.009 w/o C and 0.0065 w/o N₂. Corrosion results for this material are shown in Fig. 17. All three samples tested in 650°F water opened up a single split in the cladding near one end while the 750°F steam samples showed a general rupture of the cladding. In examining the more drastic failures it is often difficult to determine just where failure initiated because of severe distortion of the cladding. The time to failure varied considerably at each test temperature. At 650°F corrosion life was 77 to 199 days. At the higher temperature failure times were correspondingly shorter but still varied considerably. The type of corrosion failure noted leads to the suspicion that some unbonding occurred during fabrication.

B. U-10 5 w/o Mo Core Alloy

Corrosion results for various nominal 10.5 w/o Mo alloys are presented in Fig. 18. Of 15 samples tested in 750°F steam, 3 failed during a 58-65 day test period, while 11 failed in less than 28 days. Only 4 samples were tested in 650°F water and 4 in 680°F water. Rod identification numbers for these samples are as follows:

Temp °F	Rod No.	Ext. No.	Corrosion Life - Days
650	55	291-7	105-119
650	56	291-7	49-56
650	57	291-8	77-91
650	7	8C1	169-183
680	11	10C2	40-56
680	12	10C2	82-96
680	37	291-7	26-33
680	41	291-8	26-33

The reported molybdenum analysis of ingot No. Y-61 (Ext. No. 291-7, 291-8) was 9.3 w/o, which, if correct, may account for the poor corrosion life of this material as compared to extrusion 8C1.

C. U-12 w/o Mo Alloy

Corrosion life as a function of temperature for as-extruded U-12 w/o Mo alloys is presented in Fig. 19A and 19B, and rod identification information is recorded in the following table:

Temp. °F	Rod No.	Ext. No.	Ingot No.	w/o Mo	w/o C	Corrosion Life, Days
650	58	291-1	Y-72	11.7	0.008	245-259
650	59	291-1	Y-72	11.7	0.008	259-273
650	60	291-1	Y-72	11.7	0.008	245-259
650	203	408-1	L-71	11.9	0.060	196
650	204	408-1	L-71	11.9	0.060	196
650	205	408-1	L-71	11.9	0.060	182-196
650	206	408-4	L-75	12.1	0.43	252
650	207	408-4	L-75	12.1	0.43	42-56
650	208	408-4	L-75	12.1	0.43	252
650	212	208-2	L-72	12.1	0.004	154-168
650	213	208-2	L-72	12.1	0.004	140-154
650	214	208-2	L-72	12.1	0.004	140-154
650	316	M03a3	J860T	-	-	154-168
650	317	M03a3	J860T	-	-	196
650	318	M03a3	J860T	-	-	196
680	41	291-1	Y-72	11.7	0.008	54-68
680	43	291-1	Y-72	11.7	0.008	96-110
680	44	291-1	Y-72	11.7	0.008	82-96
680	133	ELR-19 Series	-	-	-	84-98
680	134	ELR-19 Series	-	-	-	14-28
680	135	ELR-19 Series	-	-	-	84-98
680	138	ELR-19 Series	-	-	-	98-112
680	227	432-5	-	-	-	70-84
680	228	432-5	-	-	-	70-84

Temp °F	Rod No.	Ext. No.	Ingot No.	w/o Mo	w/o C	Corrosion Life, Days
680	229	432-5	-	-	-	56-70
680	230	432-5	-	-	-	56-70
680	231	432-5	-	-	-	70-84
750	79	291-1	Y-72	11.7	0.008	14-21
750	155	408-1	L-71	11.9	0.060	21-28
750	156	408-1	L-71	11.9	0.060	21-28
750	157	408-1	L-71	11.9	0.060	21-28
750	161	408-4	L-75	12.1	0.43	0-7
750	162	408-4	L-75	12.1	0.43	0-7
750	163	408-4	L-75	12.1	0.43	7-14
750	158	408-2	L-72	12.1	0.004	21-28
750	159	408-2	L-72	12.1	0.004	21-28
750	160	408-2	L-72	12.1	0.004	21-28
750	309	MA-303	J-860-T	-	-	49-63
750	310	MA-303	J-860-T	-	-	35-42
750	311	MA-303	J-860-T	-	-	42-49

Note that there is a considerable variation in the carbon content of the various ingots. Ingots Y-72 and L-72 were melted from derby uranium in BeO or MgO crucibles while L-71 and L-75 were made from HEW graphite melted stock. Ingot L-71 was melted in a BeO crucible, and L-75 was melted in a graphite crucible which accounts for its exceptionally high carbon content. Examination of the above table for these materials indicates that there is no correlation between corrosion life and carbon content of the core alloy.

From Fig. 19A it can be seen that only one sample tested in 650°F water failed in less than about 147 days. This sample (No. 207) was made from the high carbon ingot but two other identical samples tested with it were unaffected after 252 days of testing. A photograph of this sample after the 42-56 day test period is shown in Fig. 20(A). The slight splitting of the cladding differs from the typical severe rupture of the cladding shown in Fig. 20(B) for No. 59 which was unaffected during the first 259 days of testing before failing in the manner shown during the next 14 days of testing.

The testing temperature has a pronounced effect on corrosion life as shown in Fig. 19A. At 750°F failures occurred early, in 0-49 days. At 680°F the range of failure time was 14 to 112 days while at 650°F the range

was 42 to 273 days. On a statistical basis 5% of the rod elements may be expected to fail within 40 days in 650°F water and within 20 days in 680°F water. Similarly, 10% failure will occur within 80 days in 650°F water and within 36 days in 680°F water.

It is apparent that the variability of corrosion life displayed by the fuel element samples must be materially reduced in order to be considered satisfactory for reactor use. In this connection it may be noted that extrusion MO3a3 stands out as being superior to the others. The samples from this extrusion had at least twice the corrosion life of others in 750°F steam and showed excellent performance in 650°F water. At the latter temperature one rod failed in 154 to 168 days and two others were still in test after 196 days. The core material for this particular extrusion was prepared differently than the others. After induction melting the cast ingot was consumably arc melted in an effort to obtain greater alloy homogeneity and minimize shrinkage porosity in the casting. This duplex method for preparing core alloys was later investigated in detail and will be discussed in Section IX.

D. U-13.5 w/o Mo Alloys

Corrosion life data for 10 samples for two extrusions of nominal 13.5 w/o Mo alloy are presented in Fig. 21. These samples were all made from ingot Y-70 which was melted in a BeO crucible and cast at 1650°C. Chemical analysis indicated 14.0 w/o Mo and 0.041 w/o carbon.

Although four of the samples did not fail, No. 63 and No. 45 were beginning to pimple at the defect at the time testing was discontinued. Sample No. 46 failed by general rupture of the cladding while No. 47 developed a hair-line crack at the weld of one end plug so that the test was discontinued.

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For the 750°F steam test only No. 81 ruptured the cladding while the other three samples were discontinued because slight general swelling was detected.

E. U-10 w/o Nb Alloys

Although only the results for the U-10 w/o Nb alloy are being reported here in detail, 5 samples of a U-4 w/o Nb alloy were tested in 650°F water and failed during the first 14-day test period, and 9 samples of a U-6 w/o Nb alloy failed in less than 28 days of testing under similar conditions. Alloys of such low Nb content are not gamma phase, but rather "strained alpha". Both U-10 w/o Nb extrusions were made from an ingot that analyzed 10.0 w/o Nb. Corrosion life data are presented in Fig. 22 for the as-extruded samples. Only one of 5 samples tested at 650°F failed and this sample (No. 64) failed as a result of a defective weld at one end plug as shown in Fig. 23(A).

The data for samples No. 331 and No. 327, which were heated at 800°C for 2 and 24 hours, respectively, are presented to show that core-clad interdiffusion does not cause as rapid corrosion failure as is the case for U-Mo alloys heated at high temperatures. The manner of failure of No. 327 has been presented in detail in Section IV, C.

The two samples tested in 680°F were dimensionally unaffected after 208 days of testing. After these samples were again placed in test, they were accidentally overheated (about 800°F for 10 hr) and at the end of the 14 day test period both had failed by rupture of the cladding.

In 750°F steam this alloy has the short corrosion life characteristic of all of the various alloys tested. At this temperature samples show localized pimpling and splitting of the cladding in the general region of the hole defects in addition to the general rupture of the cladding which evidently followed the initial splitting. This condition is shown in Fig. 23(B) and (C) for the two 10 w/o Nb samples tested. Thus, the indication is that the

corrosion rate of all alloys is so high at this temperature that a simple oxidation of the core alloy is the controlling factor in corrosion failure.

F. U-Mo-Nb Alloys

Seven ternary alloys were melted and 5 of these were extruded directly to about 0.5 in. and only 2 to 0.31 in. diameter. This difference in rod diameter is not believed to be of great importance in the corrosion life of elements. Corrosion life data for these materials are presented in Fig. 24A and 24B. Only one of the alloys, 10 w/o Mo + 1.5 Nb, shows exceptional corrosion resistance. The No. 106 rod of this alloy, tested in 650°F water for 308 days, was cross sectioned and examined and showed no evidence of pimpling at the hole defects. The 680°F test sample (No. 118) was accidentally overheated (800°F for 10 hr) after 181 days and was continued in test in 650°F water. It later failed after accumulating a total test time of 224-238 days.

G. U₃Si Alloys

Two extrusions of U-3.8 w/o Si alloy (U₃Si) were made from material machined from castings of induction melted alloy. These were ingots 405-2 and 405-5 extruded to 0.314 in. diameter. Examination showed good clad-core bonding except for a few longitudinal void stringers at the interface. Element specimens were made, epsilonized for 20 hours at 800°C, and then holes were drilled in the standard manner. All 6 samples tested in 650°F water failed at the end plug welds in less than 7 days of testing.

New samples were prepared with a longer (1/2 in.) plug so that the heat effects on the uranium alloy during welding would be less pronounced. Although end plug rupturing was eliminated these samples showed a uniform swelling after 7 days in 650°F water and burst the cladding during the next 7 days of testing. This type of failure is due to corrosion of the core-clad diffusion layer formed during the epsilonizing heat treatment.

NO. 405-2

To determine if less annealing would produce longer element life, identical element specimens were annealed at 800°C for 0, 1/2, 1, 4, 8-1/2, 16 and 20 hours and then tested in 650°F water. All elements failed in less than 7 days. As shown in Fig. 25(3) those annealed for at least 16 hours showed the least catastrophic failure. For these samples, large relatively unaffected pieces of the alloy remain within the cladding indicating that epsilonization of the core alloy was attained. However, general swelling and splitting of the cladding was caused by rapid corrosion of the diffusion layer that was formed during the anneal. Most recent efforts of the Fuel Element Subdivision have been to epsilonize the U-Si castings for 7 days at 800°C before extrusion and then to extrude at a temperature not over 925°C in order to preserve this phase.

Three duplex-melted ingots were epsilonized, prior to extrusion, at 800°C for 7 days, and coextruded with Zircaloy-2 cladding. Duplex melting techniques were used to minimize alloy segregation. Extrusion temperatures were varied to investigate the effect of temperature on core-clad inter-diffusion. Fuel elements were fabricated, defected with 0.040 in. diameter holes and corrosion tested in 650°F degassed water. The corrosion test results together with the metallographic and extrusion information are listed in the following table:

Ext. No.	Ext. Temp. °C	Residual Phases	Corrosion Life - Days
26-1	843 (1550°F)	alpha + delta	0 - 28
27-1	871 (1600°F)	alpha + delta	0 - 56
28-1	899 (1650°F)	delta	0 - 28

From the results listed above, it is apparent that samples of U-3.8 w/o Si clad with Zircaloy-2 by coextrusion are subject to rapid attack in 650°F water at the core-clad interface. It has definitely been established by X-ray diffraction studied on samples which were heat treated to form thick interdiffusion layers that two important layers form. One of these layers is the silicide of Zirconium, $ZrSi_2$, formed on the clad side of the interface; the other layer is alpha-uranium, formed on the core side of the interface. The presence of the alpha-uranium layer adjacent to the core alloy is believed to be responsible for the bond-line attack. The alpha-uranium layer is formed by the migration of Si from the U_3Si core into the Zircaloy-2 clad leaving a region deficient in silicon that transforms to alpha-uranium. These diffusion layers can be seen in Fig. 26. The identification of the zones illustrated are listed below:

1. Zircaloy-2 cladding.
2. Zone 1, the layer below the cladding (Widmanstätten structure), is essentially zirconium with lattice constants corresponding to those of Zirconium.
3. Zone 2, immediately below Zone 1, is $ZrSi_2$.
4. Zone 3, adjacent to the core alloy, corresponds to alpha uranium.
5. Epsilon (U_3Si) core.
6. Matrix of epsilon and delta (U_3Si_2).

It is apparent from this that fuel elements prepared by direct bonding of Zircaloy-2 to U_3Si will be subject to rapid bond-line attack unless a barrier layer is interposed between the cladding and core. The primary requirement of such a barrier layer is that it does not form a silicide. Evidence for this was confirmed by corrosion tests of elements

prepared with aluminum, niobium and molybdenum barriers interposed between the Zircaloy-2 and U_3Si . Niobium and molybdenum form silicides and bond-line attack occurs at the core-barrier interface. Aluminum does not form a silicide and no bond-line attack occurs when this material is used as a barrier. Aluminum was first indicated as offering promise as a barrier layer in pressure bonded samples prepared and tested by Sylvania Electric Products under Subcontract No. 73-(14-383) Task C-17.⁹ Extensive development work is now being carried out on U_3Si alloys and will be completely covered in a separate report.

VII. Effect of Low Temperature Annealing on Corrosion Life

In the case of bare samples of gamma phase alloys it was found that a low temperature annealing treatment in the range of 343 to 400°C, following the high temperature (900°C) gamma homogenization treatment, significantly improves corrosion life. This will be discussed in detail in Part III of this series of reports. For clad rods it has already been shown that the gamma homogenization treatment cannot be applied without deleterious core-clad interdiffusion. Assuming, therefore, that the coextruded rods were sufficiently homogeneous, several sample elements containing U-Mo and U-Nb core alloys, were subjected to a low temperature anneal at either 343 or 400°C for 5 weeks, without benefit of the gamma quench, and exposed through the 0.040 in. diameter defect to 650°F water and 750°F steam.

The results of these tests are included in Figs. 27 and 28. Comparison of the corrosion data for the annealed samples and previously reported data on samples from the same extrusions without annealing indicate that 943°F annealing produces no significant changes. Samples annealed at 400°C, however, displayed markedly reduced corrosion life in all cases except samples with a U-10 w/o Nb core alloy. Annealing at this temperature

resulted in some transformation of the corrosion resistant gamma phase in as-extruded material to corrodible alpha plus epsilon. In the case of U-12 and -13.5 w/o Mo, however, well-homogenized samples annealed 5 weeks at 400°C are in the early stages of transformation as shown in thermal transformation studies at 343°C by Armour Research Foundation under Task 6 of Subcontract 73-(14-309).¹⁰ A small amount of isolated transformation product was not expected to markedly reduce corrosion life. It is suspected that other factors, such as alloy segregation in the extrusions, resulted in enhanced transformation upon subsequent annealing and was a major factor in reducing corrosion life. The U-10 w/o Nb samples on the other hand, are less thermally stable than U-12 w/o Mo. The fact that corrosion life did not deteriorate in this case, suggests that the defect was not drilled completely through the cladding. This condition was found in other samples which exhibited exceptionally long life (Section IX, D) and may explain the findings in this experiment.

VIII. Effect of Various Cladding Variables

From the corrosion mechanism postulated in Section IV, B it would be expected that corrosion life of gamma phase uranium alloys would be a function of the exposed area to volume ratio of the samples. In the case of Zircaloy-2 clad rods this requires the absence of corrosion at the interface. It was desirable, therefore, to determine the amount by which corrosion life would be decreased when the area of exposed fuel is substantially increased. It was previously shown that Zircaloy-2 was very effective as a hydrogen getter when 0.040 in. diameter holes are drilled through the cladding. In this case the amount of corrosion hydrogen absorbed and remaining in the core alloy is less than the solubility limit (25 ppm) even after very long (over 300 days) exposure to 650°F water since no

hydride precipitation is observed. This is consistent with thermodynamic calculations which indicate that Zircaloy-2 in contact with gamma phase alloys will absorb the majority of the hydrogen released during corrosion until it becomes saturated with hydrogen. This will be discussed more thoroughly in Part III of this series of reports.

Of importance, also, is the determination of effects produced by different thicknesses of cladding and different types of end plugs. If thin cladding is used it might be expected that the pimpling type of failure due to oxide build-up at the base of the defect might be more prevalent. If corrosion occurs rapidly at the core-clad interface a thin cladding would rupture early. In the case of thicker cladding, this type of attack may proceed rapidly to the end plug regions and cause failure to occur at the ends of the samples. Thus, the design of end plugs may be of importance in controlling the method by which the fuel element ultimately fails.

Although not investigated in detail, some data on the effects of defect size, cladding thickness and design of end plugs were obtained, and are presented below.

A. Effect of Defect Size

The closest approach to determining the effect of the presence or absence of cladding has been in the case of the U-10 W/o Nb alloy extrusion No. 405-9 in which the cladding was removed by machining in order to test the alloy in the bare condition. Samples so produced were 1/2 in. long and slightly less than 0.250 in. in diameter. Results for these bare samples tested in 650°F water are presented in Fig. 29. Data for the clad elements presented in Section VI, E, cannot be compared directly with the bare samples because none of the 4 satisfactory samples failed after 252 days of testing.

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Even the samples showing bond-line attack as a result of annealing at 800°C for 24 hours failed only after 112 days. The much longer corrosion life of the gamma annealed bare samples over the as-extruded bare samples is an indication that corrosion resistance of clad samples would be further improved by annealing if core-clad interdiffusion could be prevented.

(not one) was
Since none of the U-Mo alloys were tested with the cladding removed, no direct measure of the cladding effectiveness can be made. However, the corrosion life of various gamma quenched 9 to 14 w/o Mo alloys tested at various temperatures in the bare condition can be used for comparison purposes. These data, extracted from the Part I report (Fig. 29, page 119) are reproduced in Fig. 30 along with the average time for failure of U-12 w/o Mo extrusion-clad sample elements taken from Fig. 19. While 750°F steam testing appears severe for both bare and clad samples, a marked improvement in corrosion life of the clad elements is apparent at each test temperature. Such a comparison is qualitative and is presented only as an illustration of the marked improvement resulting from cladding.

More quantitative data were obtained by introducing various size defects in fuel element samples prepared from a single U-12 w/o Mo rod coextruded with Zircaloy-2 cladding. Four samples each were prepared with 0.003 in., 0.013 in., 0.020 in., 0.040 in. and 0.080 in. diameter defects. Corrosion tests in 650°F water indicated that all 4 elements with 0.080 in. defects failed in 70 to 126 days. Two of 4 elements with 0.040 in. defects failed in 84 to 98 days. One of 4 elements with an 0.020 in. defect failed in 154 to 168 days. None of the other elements have failed in 182 days of test.

A similar experiment was performed on a single element in which 3 different sized holes (3/16 in., 1/8 in. and 1/16 in. diameter) were drilled through the cladding. After 28-35 days in 650°F water the cladding

split at the largest hole. An identical element with 0.040 in. diameter holes ruptured the cladding during 49-56 days of testing.

In another experiment, involving induction melted U-9 w/o Mo core alloy coextruded with Zircaloy-2 cladding, slots of various sizes were introduced in the cladding of a single simulated fuel element.

- a) A longitudinal 0.015 in. x 1.2 in. slot near one end
- b) A transverse 0.015 in. x 0.7 in. slot near the other end
- c) A 0.040 in. diameter hole in the center of the element diametrically opposite the slots.

This element was tested in 650°F water and examined and weighed after each 7 or 14 day test period. Weight measurements during the first 82 days of testing indicated a weight loss (based on the alloy surface area exposed) of about 0.17 mg/cm²/hr. However, such measurements may be misleading because of inability to estimate accurately the uranium alloy surface area exposed after extensive testing and to evaluate accurately the relative amounts of uranium-oxide lost in the water and that trapped in the defects. The condition of the sample is shown in Fig. 31A after 115 days of testing.

During the next 14 day testing period rupturing in the vicinity of the longitudinal slot occurred as shown in Fig. 31B. The ends of the slot are still visible and a uniform swelling and longitudinal splitting of the cladding occurred in the back side as well as in the photographed front side of the rod. The ruptured end was removed and the open end again fitted with a plug. The transverse slot failed as a result of cracking of the uranium alloy during the next 14 day test period. The slot opened about 10° causing an angular bend in the bar. This end was also removed, a new end plug welded in place, and the test continued for an additional 24 day period (167 days total test time). During this last test period failure of

the newest end plug weld because of contamination during welding caused such damage to the 2-1/2 in. long element that testing was discontinued. Examination of cross sections in the general vicinity of the drilled hole showed that no cracking occurred in these regions. Microstructure of the uranium alloy at the bottom of the corrosion cavity shows an equi-axed grain structure and no hydride phase. Hardness increased from about 350 DPH initially to about 540 DPH after the test because of some transformation during testing. Finally, an intact 1/2 in. length of the failed rod cut from a section near the drilled hole was tested in 650°F water without plugging the ends. After 7 days the exposed uranium alloy showed only an adherent oxide scale but after an additional 7 days of testing considerable cracking of the alloy had occurred.

The ratio of exposed alloy surface area for the longitudinal slot, the transverse slot and the hole was 18:10:1, respectively. Failure was noted in the order given above. However, the respective times for failure were by no means in the ratio given above. Note that although the total area exposed was about 30 times that exposed in case of a typical 40 mil defect, failure times were by no means appreciably shorter. Thus it appears that size of defect affects corrosion life, but the quantitative relation is not obvious. Also defect shape is apparently of some influence on corrosion life. These variables were eliminated from the evaluation of the various alloy rod elements since the defect was standardized at a 0.040 in. diameter hole.

B. Effect of Cladding Thickness

For reactor design purposes it was important to establish any effect of the thickness of Zircaloy cladding on corrosion life. For these tests Uel2 w/o Mo core alloy induction melted and extruded directly to 0.31 in. diameter and with a nominal 0.030 in. cladding thickness was machined to

produce 0.010 in. and 0.020 in. cladding thickness. The standard 0.040 in. diameter hole was drilled through the cladding at the center of each simulated fuel element sample. Corrosion results for 650°F water and 750°F steam testing are presented in Fig. 32. Only 2 of 7 samples tested in water failed after 196 days of testing so that it can be concluded that cladding thickness is unimportant under these conditions. In steam there is an indication of slightly longer life with the thickest cladding.

C. Effect of Type of End Plug

Since some of the simulated fuel elements failed by swelling and rupturing the cladding in the vicinity of the end plugs, even though the hole defects were drilled through the cladding at the center of the elements, experimental samples were made in which the type of end plugs was varied. Samples of U-12-wA Mo core alloy extruded directly to 0.31 in. diameter and with a 30 mil cladding were tested in 650°F water. The corrosion life data are shown in Fig. 33. The numbers in column 2 signify the type of end plug on each end of the elements corresponding to the types identified in Fig. 34. Type No. 1 is the standard plug used for all routine elements. Type No. 2 and No. 3 were designed to test the effect of keeping the heat generated during welding away from the uranium alloy. The core alloy in the latter designs was 1 in. from the weld rather than the 1/4 in. in the standard end plug. Since swelling at the base of the end plug was common (particularly for high temperature annealed samples) in routine failures, types No. 1A and No. 3A were intended to show if such heat-induced corrosion swelling occurred in No. 1A and was absent in No. 3A for samples in which the water did not penetrate along the bond line. In No. 2A a space for the corrosion product was provided.

Examination of the results in Fig. 33 show that the above questions were not answered. Nine of the 15 samples tested split the cladding near the hole drilled in the center of the rod, two did not fail after 224 days of testing, and only four showed failure near the ends of the samples. Of the seven samples in which a hole was drilled through an end plug, one sample showed swelling near a No. 1A end plug, while two burst at an end opposite a drilled plug. A longitudinal section through the No. 3A end of sample No. 293 showed no bond line corrosion or corrosion at the corners of the uranium alloy. The reason for this and three other samples splitting the cladding near the center hole when a much larger alloy surface at one end is exposed to the water is not known. This constitutes, however, additional evidence that defect size is unimportant compared to other factors influencing corrosion life.

IX. Corrosion Life Data for Coextruded Rod Elements
Prepared With Various Duplex Melted Core Alloys

From fuel element evaluation tests presented in Section VI it was apparent that considerable variability was obtained in the corrosion life of coextruded rod elements prepared with various gamma phase core alloys. Also much of the preceding data were obtained before a reliable fabrication method had been developed. Thus the subsequent data are presented in much more detail and indicate that much of the variability previously encountered was influenced by unrecognized factors in the fabrication process. These later data indicate little variability of corrosion life. In this section several factors which conceivably might be responsible for such variability as may exist are presented. One of these factors, suggested in the previous section, involved melting practice. It was indicated that alloy segregation and center porosity, prevalent in induction cast ingots, might vary from

ingot to ingot and contribute to the variability of corrosion life of the core alloys. To minimize this effect the melting procedure was changed to include remelting the induction cast ingots in an arc furnace having a water-cooled copper crucible. The induction-cast ingot served as a consumable electrode in this operation. Ingots produced in this way were quite sound and less subject to alloy segregation.

Several gamma phase alloys prepared as duplex melted ingots were coextruded with Zircaloy-2 cladding to about 0.50 in. diameter rods. These alloys included U-10.5 and U-12 w/o Mo, U-8, -10 and -12 w/o Nb and ternary alloys of U-Mo-Pt and U-Nb-Pt. Additions of platinum were made to some of the binary alloys to take advantage of the prolonged corrosion life experienced with bare samples containing this element. This was previously discussed in Part I of the report series. Half of each coextruded rod was cold drawn. The reduction of area by cold drawing varied in the range of 15 to 56% for different extrusions. Cold drawing was introduced as another variable because it was desirable, from a production standpoint, to facilitate fabrication to final size and avoid the necessity of using two extrusion operations in production. Chemical analysis and fabrication information for the 20 extrusions involved in this study is included in Fig. 35.

In an effort to improve homogenization of the core alloy without resorting to barrier layers, the effectiveness of a gamma phase heat treatment was investigated on duplex melted ingots prior to extrusion. Work along these lines was limited to U-12 w/o Mo as the core alloy. Also, the effect on corrosion life of low temperature stress-relieving and recrystallization treatments was investigated on extruded and cold drawn rods of this alloy.

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In continuation of the study designed to minimize corrosion attack at the core-clad interface, the possibility of employing barrier layers, which showed promise in earlier tests, was investigated in greater detail. Duplex melted ingots of U-10.5 w/o Mo and U-10 w/o Nb were employed as core materials. Barrier materials included molybdenum, niobium, platinum, palladium and alloys of U-Mo-Pt and U-Nb.

Except for special cases involving tests of bare-end samples, 3 in. long defected fuel element samples were corrosion tested in 650°F degassed water. The samples were tested in each of the following conditions:

As-extruded

As-cold-drawn

Extruded plus gamma quenched*

Cold-drawn plus gamma quenched*

Extruded plus gamma quenched plus annealed**

Cold-drawn plus gamma quenched plus annealed**

* 900°C for 24 hours followed by water quenching

** 400°C for 5 weeks followed by water quenching

The heat treating operations were carried out in evacuated and sealed Vycor tubes. Gamma quenching was designed to investigate bond-line attack and the effectiveness of barrier layers in preventing this type of attack. Annealing at 400°C was shown to improve the corrosion resistance of the core alloy when tested in the bare condition. It was introduced into this investigation to determine if it would be effective in clad material especially when applied to cold-drawn rods.

A. U-10.5 w/o Mo Core Alloy

Ingot No. J-843 with an analysis of 10.5 w/o Mo and 0.016 w/o C was consumably remelted and extruded clad at 865°C to a diameter of 0.465 in. Half the extrusion was cold drawn to 0.325 in. diameter. Corrosion results for simulated fuel elements containing a 0.040 in. diameter defect are shown

in Fig. 36. Five of six samples tested in the extruded condition have 182 days of test time in 650°F water. One sample failed in 168 to 182 days. This can be directly compared with the variability of failure time of 56 to 176 days of the induction cast and directly extruded rods shown in Fig. 18. The 5 cold drawn rods all failed in less than 28 days by general rupture of the cladding. The failure by rupture initiated near the end cap indicating bond-line attack at the core-clad interface. Possibly, cold-drawing weakened the core-clad bond. Metallographic examination of cold-drawn material indicated that this was a definite possibility. Subsequent heat treatment, however, caused core-clad interdiffusion indicating that the bond was not ruptured by cold-drawing.

B. U-12 w/o Mo Core Alloy

1. Effect of Duplex Melting and Cold Drawing

Extrusions MO3Al-1 and MO3Al-3 were fabricated from induction cast ingot J-848 which analyzed 12 w/o Mo and 0.046 w/o C. The ingot was consumably arc melted and two sections coextruded with Zircaloy-2 to a diameter of 0.460 in. Half of each extrusion was cold-drawn to 0.325 in. diameter (48% area reduction). The corrosion life data of defected fuel elements are presented in Fig. 37A and 37B. As in the case of the as-extruded U-10.5 w/o Mo rods, no failures were observed after 182 days of test in 650°F water. These samples, which indicate quite good corrosion life and consistency of corrosion life, are continuing in test.

The cold-drawn samples all failed in 0-14 days. Failure occurred by bond-line attack and subsequent fuel disintegration. Sample rods, heated 24 hours at 900°C and water quenched, failed in 14 - 28 days, failure again occurring by bond line attack. Direct evidence of bond-line attack was obtained by corrosion testing bare end samples. Fig. 38 illustrates the

progress of bond-line failure in a cold-drawn and gamma quenched sample after 7 days in 650°F water. The bond was rapidly attacked at the bare end and attack progressed down the diffusion layers adjacent to the core alloy. The attacked layers correspond to those referred to in Section IV, B.

2. Effect of Homogenization Prior to Extrusion

Metallographic examination of duplex melted and coextruded rods indicated that alloy segregation is not eliminated by duplex melting. The cored structure in the ingot results in longitudinal stringers representing concentration gradients. These are illustrated in Fig. 39A. When bare samples are corrosion tested in 650°F water, the stringers are preferentially attacked and lead to early failures of a fibrous nature with longitudinal cracking. This effect of homogenization will be discussed in detail in Part III under "Mechanism of Corrosion".

In the case of clad extrusions interdiffusion of core and clad, shown to result in bond line attack, precludes a homogenizing heat treatment. Therefore, the feasibility of homogenizing the duplex melted ingots prior to extrusion was investigated. Fig. 39B showing the microstructure of a pre-homogenized duplex melted ingot, after extrusion, indicates that the pre-homogenizing treatment was effective in eliminating the stringers. Accordingly, one of 2 U-12 w/o Mo billets from duplex melted ingot J-875 was homogenized for 48 hours at 1000°C prior to coextrusion. The other billet was coextruded without benefit of prehomogenization. The microstructures shown in Figs. 39A and 39B are representative of these extrusions.

The results of corrosion tests in 650°F water for defected fuel element samples from the two extrusions are given in Fig. 40A and 40B. It will be noted that both the samples fabricated from prehomogenized and non-prehomogenized billets have withstood satisfactorily 210 days of test

and are continuing in test. While the effectiveness of prehomogenization may show up later, it is apparent that the segregation which shows a marked adverse effect on bare extrusion samples is not a major factor controlling variability in clad samples. Also, it may be inferred from this that the variability of corrosion life previously observed for induction cast and coextruded rod samples of U-12 w/o Mo probably was not caused by stringer-type segregation.

Additional samples from these extrusions were corrosion tested after annealing for 5 weeks at 400°C and 1 week at 500°C. Of the former, as shown in Fig. 40A, one sample is still in test after 147 days, while another failed in 21-35 days, apparently because of incomplete bonding of core and cladding. Early failure of samples annealed at 500°C (7-21 days) is attributed to transformation of the gamma phase core alloy to the corrodible alpha plus epsilon phases.

3. Effect of Varying Amounts of Cold Drawing

It was previously shown that defected rod samples of U-12 w/o Mo coextrusions cold drawn 48% reduction in area fail rapidly in 650°F water even when the extrusions are prepared from duplex melted ingots. To determine if lower cold drawing reductions can be tolerated sections of the two extrusions made from ingot J-875, described above, were cold drawn 17 and 30% reduction in area. Defected rod samples were corrosion tested in the cold drawn conditions and also in the annealed (400°C for 8 weeks and 500°C for 1 week) conditions. Results are shown in Fig. 40B.

As in the case of as-extruded samples, the cold drawn samples have withstood 210 days of test in 650°F water. One prehomogenized sample, cold-drawn 30%, has failed in 168-182 days. Thus, cold drawing 17 and 30% does not appear to damage seriously the core-clad bond or impair corrosion

life. Cold drawing, however, may hasten transformation of the gamma phase since samples annealed at 400°C fail earlier with increasing amounts of cold work. The samples annealed at 500°C fail very early (7-21 days) irrespective of cold work or prehomogenization of ingots.

4. Feasibility of Annealing Cold Drawn Rods

Since large amounts of cold drawing (48% R.A.) were found to be detrimental to corrosion life and smaller amounts (17 and 30% R.A.) may hasten transformation of the gamma phase, the possibility of eliminating the effects of cold work by a stress relief and recrystallization anneal was investigated. This was first done using two Zircaloy-2 clad extrusions fabricated from an induction melted ingot (No. F-1505), of U-12 w/o Mo after homogenizing at 900°C for 48 hours. The extrusions were cold drawn 53% and 40% reduction in area and fuel element samples prepared. Prior to introducing the defects the samples were annealed at temperatures of 700, 800 and 900°C for time periods varying from 10 minutes to 24 hours. Thus, temperatures and times sufficient to cause stress relief and recrystallization without excessive growth of diffusion layers were included in the investigation.

The results shown in Figs. 41A and 41B indicated considerable variability of corrosion life for the samples cold drawn 53%. This was attributed to center porosity observed in the extrusions. However, it appeared that the optimum heat treatment involved 600°C for about 8 hours or 700°C for 10 to 30 minutes. Based on this the samples which received 40% cold work, shown in Fig. 41C, were annealed for 30 minutes to 8 hours at 600°C and 5 to 30 minutes at 700°C. One sample annealed at 600°C for 30 minutes failed in 42 to 56 days. No other failures have occurred in 70 days of test. The test time, however, is too short to draw any definite conclusions.

Because of the center porosity in the first extrusions the tests were repeated using a duplex melted ingot which was prehomogenized in the same way as the induction cast ingot, coextruded and cold drawn 53% reduction in area. The corrosion life data and heat treatments are listed in Figs. 42A and 42B. While the accumulated test time (112 days) is insufficient to draw definite conclusions, it again appears that a short time anneal, 5 to 10 minutes at 700°C, shows promise of eliminating the deleterious effects of cold work without causing excessive bond-line attack and excessive growth of corrodible interdiffusion layers. The appearance of the interdiffusion zones of as-extruded, cold drawn and cold drawn and annealed samples, shown in Fig. 43 appears to substantiate this.

C. U-8 w/o Nb Core Alloy

Induction cast ingot No. J-840, having an analysis of 8.25 w/o Nb and 0.016 w/o C, was consumably arc-melted and coextruded with Zircaloy-2 cladding to 0.475 in. diameter. Sections of the extruded rod were cold drawn 39 and 53% reduction in area and tested as defected fuel elements in various conditions of heat treatment. Results are shown in Fig. 44. Although elements prepared from this core alloy did not exhibit outstanding corrosion life, it appears that homogenization at 900°C of as-extruded samples does not produce as severely corrodible core-clad interdiffusion layers as was found for U-Mo alloys. When failure occurs, however, it is by bond-line attack. Annealing at 400°C rapidly transforms the gamma phase. This is reflected in the decreased life of gamma quenched and annealed samples. All as-cold-drawn samples failed in 0-14 days by severe rupture of the cladding and complete disintegration of the fuel. Homogenizing after cold drawing improved corrosion life but did not make it comparable with as-extruded material.

D. U-10 w/o Nb Core Alloy

Three induction melted ingots were consumably arc-melted and coextruded with Zircaloy-2. The analyses and extrusion identifications are recorded in the following table:

<u>Ingot No.</u>	<u>Ext. No.</u>	<u>Ext. Temp.</u>	<u>w/o Nb</u>	<u>w/o C</u>
J 851	MO3A2-4	1750°F	10.5	0.019
J 852	MO3A2-5	1675°F	10.1	0.021
J 842	MO3A2-11	1595°F	10.2	0.017

Note the considerable variation in extrusion temperature. Half of each extrusion was cold drawn 50% reduction in area. The defected fuel element corrosion life results for extruded rods are presented in Fig. 45, and the cold drawn results are shown in Fig. 46A and 46B.

Five as-extruded elements have failed, one in 84-98 days, and another four in 126-196 days, while one remains in test after 210 days. Cold drawn elements failed rapidly in 0-14 days, at the end of which time the fuel was found to be completely disintegrated.

Heat treatment at 900°C for 24 hours appears to be detrimental when compared with the as-extruded corrosion life and beneficial compared with the cold drawn samples. The heat treated cold drawn samples show a variability of corrosion life not found in the extruded samples. Heat treated samples in both conditions fail in the interdiffusion zone between core and clad. Fig. 47 shows photomicrographs of the diffusion zone in the extruded and cold drawn samples heat treated at 900°C for 24 hours and the effect of corrosion on clad bare-end samples after this heat treatment.

Elements which have been given a double heat treatment (annealed at 900°C for 24 hours then aged for 5 weeks at 400°C) have shown a surprisingly long life in view of the short life (0-3 days) of bare fuel treated in this

manner. The cold drawn samples continue to show corrosion life variability after the double heat treatment. In order to examine the progress of corrosion after annealing and aging, one cold drawn sample was removed from test for microexamination after 28 days and an extruded element was removed after 56 days of test. Fig. 48A clearly shows the progress of corrosion at the defect of the cold drawn element. The photomicrograph indicates that the Zircaloy cladding was partially transformed from alpha to beta during the high temperature treatment. Below the cladding are at least three core-clad interdiffusion layers which apparently corrode at different rates. The thick layer, adjacent to the Zircaloy has a Widmanstatten structure. This layer which is high in zirconium and low in uranium and niobium corrodes faster than the layers below it. Next to this layer is what appears to be a hard brittle layer with a columnar grain structure. Below it is another layer adjacent to the core alloy which appears to have better corrosion resistance since the corroding section has a diameter at least as small as that of the partially transformed Zircaloy cladding. While the compositions of each layer are not now known, it is probable that the corrosion resistant layer is a ternary alloy of U-Nb-Zr with a Nb content somewhat below 10 w/o and a relatively low Zirconium content. The core itself has an X-ray determined structure consisting mostly of alpha with some gamma. This photomicrograph confirms the observation that in spite of considerable transformation to alpha, sufficient to ruin completely the corrosion resistance of bare samples, clad samples still show appreciable corrosion life.

Fig. 48B shows a defect in the extruded and double heat treated sample which was not machined completely through the diffusion zone. Corrosion did not progress far in 56 days, apparently confining itself to the diffusion layers. The relatively good corrosion resistance of these layers confirms

the findings for the cold drawn sample of Fig. 48A. Failure to defect completely through the hard diffusion zone may explain the long corrosion lives of the extruded and doubly heat treated samples compared to extruded and gamma quenched samples. It may also explain some of the variability observed in cold drawn and heat treated samples. Comparison of Fig. 48A with 48C (U-8 w/o Nb core sample fabricated and heat treated in the same way) indicates that the core alloy of lower niobium content is less corrosion resistant.

E. U-12 w/o Nb Core Alloy

Induction melted ingot J-915 with an analysis of 12.15 w/o Nb and 0.025 w/o C was arc melted and coextruded with Zircaloy-2 cladding. Half of the extrusion was cold drawn 56% reduction in area. Corrosion life data are listed in Figs. 49A and 49B.

The extruded rods have a corrosion life greater than 182 days in 650°F water. When gamma quenched (900°C for 24 hours) failures by bond-line attack were observed in 112 to 140 days. Gamma quenched and low temperature annealed (400°C for 5 weeks) samples have not failed in 154 days of test. All samples tested in the cold drawn condition failed early, within 56 days. Gamma quenching improved the life of the latter, but failures were again by bond-line attack. A representative failure is shown for rod sample No. 632 in Fig. 50. Also shown is the appearance of the core-clad bond zone for the cold drawn and gamma quenched material. The cold drawn, gamma quenched and annealed samples are still in test after 154 days, as is the case for extruded samples heat treated in the same way.

While test data are not complete it is apparent that rods prepared with U-12 Nb core alloy display less variability and greater promise when cold drawn and heat treated than similar binary alloys of lower niobium content.

F. U-Mo and U-Nb Core Alloys Containing
Ternary Additions of Platinum

The addition of relatively small quantities of platinum to U-Mo and U-Nb gamma phase alloys improves the corrosion resistance of bare samples. Platinum apparently acts as a hydrogen depolarizer, reducing the amount of corrosion hydrogen absorbed by the alloy. It also imparts greater thermal stability to the gamma phase. These effects of platinum will be explained in detail in Part III under "Corrosion Mechanism". To determine the effectiveness of the platinum addition in clad samples several extrusions were prepared with U-Mo and U-Nb core alloys containing intentional platinum additions. These are described below.

1. U-8 w/o Mo-1 w/o Pt Core Alloy

A duplex melted ingot with an analysis of 8.0 w/o Mo, 1.02 w/o Pt and 0.012 w/o C was coextruded with Zircaloy-2 to a diameter of 0.460 in. Half of the extrusion was cold drawn 48% reduction in area. Metallographic examination indicated that the core-clad bond was good in the as-extruded material but the bond was broken on cold drawing. This is reflected in the poor corrosion life of defected fuel element samples prepared from the cold drawn rod (Fig. 51A and 51B). The extruded samples show a satisfactory life of greater than 210 days in 650°F water. This compares favorably with data on binary U-9 w/o Mo extrusions indicated in Fig. 17. Heat treatment of the extruded material, however, results in early failure by severe attack in the diffusion zone. Thus, the platinum addition may improve the corrosion resistance of the core alloy but does not eliminate formation of corrodible core-clad interdiffusion layers upon heat treatment after extrusion.

2. U-12 w/o Mo-0.5 w/o Pt Core Alloy

A duplex melted ingot, J-825, with an analysis of 12.15 w/o Mo, 0.54 w/o Pt and 0.015 w/o C, was coextruded to 0.465 in. diameter and half of the extrusion cold drawn 50% reduction in area to 0.325 in. diameter. Corrosion life data on defected fuel elements are included in Fig. 52A and 52B. The extruded samples have a satisfactory life of over 210 days while cold drawn samples all failed in 0-14 days. Heat treatment of extruded samples reduced corrosion life and failures again occurred by bond-line attack. Heat treatment of cold drawn material improved corrosion life. Failures of these samples also occurred at the core-clad bond. However, cold drawn and heat treated samples containing the binary U-12 w/o Mo as the core material fail earlier within 28 days, as compared to 56 to 112 days for the platinum bearing core alloy. Thus, platinum has a beneficial effect in reducing core-clad bond attack but does not eliminate this type of failure in heat treated samples. The core-clad interdiffusion zones formed with U-Mo-Pt alloys are shown in Fig. 53 together with a cold drawn bare end sample which failed through the diffusion zone after 7 days in 650°F water. When compared with the U-8 w/o Mo-1 w/o Pt alloy, the U-12 w/o Mo-0.5 w/o Pt alloy shows superior corrosion properties in all conditions of heat treatment.

3. U-10 w/o Nb-1 w/o Pt Core Alloy

Induction melted ingot J-870, analyzing 10.5 w/o Nb, 1.35 w/o Pt and 0.062 w/o C, was arc melted and coextruded. During cold drawing of half the extrusion, it broke in two portions. One of these, which had received 15% reduction in area, could not be drawn further because it was too short. The other portion was further reduced so that it received 30% cold work. The corrosion life data for defected fuel element samples is included in Fig. 54.

The as-extruded and 15% cold drawn samples are still in test after 210 and 182 days, respectively. This confirms the previously indicated findings that relatively small amounts of cold work are not detrimental unless the samples are later heat treated. Extruded and cold drawn bare end samples of this material have also survived more than 98 days in 650°F water. Gamma quenching of extruded fuel element samples, however, have reduced corrosion life (70-112 days) and indicate bond line attack. Low temperature annealing further reduces life. As in the case of U-Mo alloys, therefore, platinum is beneficial in improving the corrosion resistance of the core alloy but does not markedly improve the corrosion resistance of core-clad diffusion layers formed on heat treatment.

G. Interface Metal Barrier Layers in Coextrusions
Prepared with Duplex Melted Core Alloys

The promising corrosion results indicated in Section V, D for coextruded fuel elements containing a molybdenum barrier between clad and core prompted further investigation of this material. The effort was expanded to include several other metallic barrier materials and several different heat treatment conditions. Instead of using induction melted core alloys, however, the core material was duplex melted to reduce alloy segregation and eliminate center porosity as previously explained. To obtain a direct comparison of barrier layer effectiveness one core alloy, U-10.5 w/o Mo, was used except in the case of one extrusion. A U-10 w/o Nb core was used in the latter with a niobium barrier because previous data indicated that less severe bond line attack occurs when U-Nb, rather than U-Mo, core alloys are directly bonded to Zircaloy-2.

The barrier materials included in this investigation were molybdenum, niobium, platinum, palladium, and alloys of U-15 w/o Mo-5 w/o Pt and U-10 w/o Nb. They were introduced in the form of 10 mil thick foil wrapped

around the 1.892 in. diameter core alloy or as a machined sleeve interposed between core and the Zircaloy-2 cladding container (2.41 in. outside diameter). After hot extrusion of the assemblies at 1600°F half of each extrusion was cold drawn. The final barrier layer thickness was 2 to 3 mils for the extruded rod and 1 to 1.5 mils for the cold drawn rod. The final cladding thickness was 45 mils and 30 mils for the extruded and drawn rods, respectively.

1. U-10.5 w/o Mo with a Molybdenum Barrier

Ingot J-888, containing 10.5 w/o Mo and 0.055 w/o C, was wrapped in 0.010 in. thick molybdenum foil and coextruded with Zircaloy-2 to a diameter of 0.460 in. Half the extruded rod was cold drawn to 0.325 in. diameter. The corrosion test results are reported in Fig. 55A and 55B.

It is apparent from Fig. 55A and 55B that the corrosion life varied considerably for each heat treatment condition and in most cases was not consistent for a given heat treatment. It was later found that the as-extruded and cold drawn rod sections were not completely bonded, partial unbonding occurred at the core-barrier and clad-barrier interfaces. Micro-examination of samples from the two ends and center of the as-extruded rod indicated that the ends were well bonded but the center was not. It should be noted in Fig. 55A that the two end sample rods, numbered 468 and 694, have relatively long corrosion lives while samples in the central portions had disappointingly short lives. For example, as-extruded rod sample No. 468 which came from one end of the extrusion is still in test after 140 days, and rod No. 694, which came from the opposite end of the extrusion, had a life of 112-126 days after gamma-quenching and annealing. Rod elements from the central portion of the extrusion failed early, 14 to 70 days, in both the as-extruded and heat treated conditions. It appears that the presence of a well-bonded molybdenum barrier may permit heat treatment after coextrusion. However, this needs confirmation on additional extrusions.

In the case of the cold drawn rods the location of unbonding could not be accurately established. It is suspected, however, that the cold drawing operation would have caused further unbonding of the partially unbonded extrusion. This could account for the short lives of the as-cold-drawn rod elements (0-28 days), cold drawn gamma-quenched and annealed elements (0-28 days) and the variable behavior of the cold drawn and gamma-quenched elements (14-140 days).

2. U-10.5 w/o Mo with a Niobium Barrier

Ingot J-886, with an analysis of 10.5 w/o Mo and 0.035 w/o C was consumably arc-melted, wrapped with 0.010 in. thick niobium foil and coextruded with Zircaloy-2 to a diameter of 0.460 in. Half the extruded rod was cold drawn 58% reduction in area with a final diameter of 0.320 in. The corrosion results are recorded in Fig. 56A and 56B. It should be noted that the as-extruded life of the elements was only 70-112 days and should be compared with the greater than 182 day life of the U-10.5 w/o Mo elements without a barrier. Examination of rod No. 466 at the defect indicated bond-line attack, failure taking place 120° radially away from the defect by means of a longitudinal split in the cladding which is typical of failure due to bond attack. Since the attack took place at the barrier-core interface, and the microexamination of the as-extruded samples revealed no apparent unbonding, the reason for attack in an area where an alloy of relatively good corrosion resistance exists is not known. The relatively short lives exhibited by the rods in the extruded and gamma-quenched and annealed condition (28-42 days) follow from the poor results of the as-extruded samples.

Fig. 57(A) and (B) are photomicrographs showing the attack at the core-barrier interface. The attack eventually exposed enough core alloy to the 650°F water to lead to early failure.

The results for the cold drawn rods are somewhat clouded by the presence of partial unbonding. The unbonded elements No. 609 and No. 642 are good examples of the detrimental effect of unbonding on the corrosion life, both having failed in 0-14 days whereas the remaining cold drawn elements had lives of 28-56 days. The cold drawn and gamma-quenched elements had lives of 28-84 days with one still in test after 140 days. The cold drawn, gamma-quenched and annealed samples all failed in 0-14 days by bond line attack. A typical photomicrograph of a cold drawn and gamma-quenched sample showing the diffusion zone of a well-bonded section can be seen in Fig. 58(A), and the attack through this zone in Fig. 58(B) and (C). Note the heavy precipitate on the fuel side of the diffusion zone and its disappearance after corrosion testing. It appears that a niobium barrier is not suitable when the core alloy is of the U-Mo type of alloy.

3. U-10.5 w/o Mo with Platinum and Palladium
Barrier Layers

Platinum and palladium were investigated as barrier layers because these elements are excellent hydrogen depolarizers. It was postulated that corrosion attack of the fuel alloy would be inhibited at the site of the defect by formation of molecular hydrogen, thus reducing the amount of atomic hydrogen available for diffusion into the core. Ingot No. J-884 with an analysis of 10.5 w/o Mo and 0.040 w/o C, after consumably arc melting, was wrapped in a 0.005 in. thick platinum foil and coextruded with Zircaloy-2 cladding to 0.470 in. diameter. Half of the extrusion was cold drawn to 0.325 in. diameter. Metallographic examination prior to corrosion testing indicated that the extruded rod was unbonded throughout its length at the barrier core interface. The cold drawn rod, however, appeared to be bonded and normal diffusion layers formed on heat treatment.

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Corrosion results, shown in Fig. 59, confirmed unbonding of extruded material since failure occurred in 0-14 days. Despite unbonding extruded and homogenized samples had extended, though still poor, corrosion lives. Cold drawn samples had appreciably better corrosion lives, but life was not consistent and attack occurred in the core-clad diffusion zone followed by rupture of the cladding due to build-up of surface oxide. The thin layer of platinum (about 1 mil) was probably unable to prevent core-clad inter-diffusion since heat treatment after cold drawing resulted in early failures (0-14 days).

In the case of the palladium barrier applied to duplex melted ingot No. J-888 (10.5 w/o Mo and 0.035 w/o C) a 10 mil foil was used and a thicker (2 to 3 mils) barrier obtained. However, the as-extruded and cold drawn rods were both unbonded at the core-barrier interface. Results of corrosion tests were generally unsatisfactory as indicated in Fig. 60.

4. U-10.5 w/o Mo with a U-15 w/o Mo-5 w/o Pt Alloy Barrier

Lack of bonding of barrier and core experienced with platinum and palladium barriers was eliminated by using a U-15 Mo alloy containing 5 w/o platinum as a barrier. This material was machined as a 10 mil thick sleeve and fitted over duplex melted ingot J-862 (10.35 w/o Mo and 0.028 w/o C) before extruding to 0.475 in. diameter. During cold drawing of half the extrusion the rod broke in two. However, a portion was drawn to 0.435 in. diameter (42% reduction in area).

The corrosion results, shown in Fig. 61, were disappointing. All samples failed in less than 84 days by attack at the core-barrier interface or diffusion zone. Failures occurred at longer times for samples receiving 16 rather than 42% cold work, but in either case life was considered unsatisfactory. Apparently, platinum does not appear promising as a barrier layer when used in the form of pure foil or alloyed with uranium and molybdenum.

5. U-10.5 w/o Mo with a U-10 Nb Barrier

Ingot J-892, analyzing 10.5 w/o Mo and 0.048 w/o C, was consumably arc-melted, fitted with a 30 mil thick sleeve of a U-10 Nb alloy and coextruded clad to 0.475 in. diameter. The cold drawn section received 57% reduction of area (0.300 in. diameter). Corrosion data are included in Fig. 62. Except for the as-extruded samples corrosion life was poor, failures occurring in less than 56 days. Two additional heat treatments, 4 hours at 800°C and 10 minutes at 900°C were tried on cold drawn material to reduce core-barrier interdiffusion. Corrosion life was definitely improved by the latter treatment (35 to 91 days) but still unsatisfactory. Growth of the diffusion layers by heating cold drawn material at 800 and 900°C is shown in Fig. 63. One as-extruded sample failed in 70-84 days while the other has a life greater than 140 days. Heat treatment of the extruded material reduced life to 28-42 days. The U-Nb barrier, therefore, was unsuccessful in permitting heat treatment after extrusion.

6. U-10 w/o Nb with a Niobium Barrier

Ingot No. J-813, with a niobium analysis of 10.3 w/o was arc-melted, wrapped with niobium foil and coextruded with Zircaloy-2. Half the extrusion was cold drawn 50% reduction in area. The corrosion life results of the extruded and cold drawn defected fuel elements are shown in Fig. 64A and 64B. It can be seen that the as-extruded, and extruded gamma-quenched elements are exhibiting a very satisfactory life of greater than 210 days with one as-extruded element failing in 196 to 210 days. It should be pointed out that none of the U-10.5 w/o Mo alloys tested have survived this long in 650°F water after heating 24 hours at 900°C. However, this alloy when given an additional anneal of 5 weeks at 400°C fails in less than 28 days. The cold drawn and cold drawn, gamma-quenched and low temperature annealed samples fail in less than 14 days. One out of four cold drawn and gamma-

quenched elements is still in test after 182 days, one other having been removed for examination after 140 days and one failed in 56 to 70 days, while the fourth sample failed in 168 to 182 days.

Photomicrographs of a cold drawn and gamma-quenched sample and the element which failed in 56-70 days can be seen in Fig. 65. The photos show the diffusion zone before and after failure. It is interesting to compare these photomicrographs with those of the U-10 w/o Nb alloy (without a barrier layer) shown in Fig. 47. All that remains of the diffusion zone in the U-10 w/o Nb alloy is the Widmanstatten structure, whereas this area of the diffusion zones of the same alloy with a niobium barrier between core and clad is practically intact. The attack in Fig. 65 does not take place through the diffusion layers on the clad side of the barrier, but attacks the area adjacent to the niobium barrier on the core side.

It is apparent, that a niobium barrier between Zircaloy-2 and U-10 Nb core is very beneficial to corrosion life. This barrier permits high temperature heat treatment of extruded rods and improves the life of cold drawn and gamma-quenched rods. Cold drawing, per se, and low temperature annealing, however, reduces corrosion life because of transformation of the core alloy to less corrosion resistant phases. For this reason the barrier layer is effective only when the corrosion resistant gamma phase is retained in the core alloy.

X. Conclusions

It may be concluded from the above that the most important factor influencing corrosion life of defected Zircaloy-clad rods of "corrosion-resistant" uranium alloys is the nature and quality of the core-clad interface. Corrodible composition ranges produced by inter-diffusion of core and cladding or unbonding resulting from uncontrolled variables in the fabrication procedure can produce failures in very short

times. Interdiffusion effects may be suppressed to some extent by use of suitable diffusion barriers; however, difficulties in fabrication prevent full exploitation of such benefits. The best results are produced by using samples in the as-extruded condition where minimum interdiffusion occurs and least opportunity is present for unbonding by subsequent treatment. The fuel element combination permitting maximum flexibility in fabrication and post-fabrication treatment consists of a U-10% Nb core, a Nb barrier, and a Zircaloy cladding.

Other factors, in decreasing order of importance which may also affect corrosion life of defected rod elements are listed below:

1. Core alloy composition and structure. In general a correlation exists between the corrosion rate of bare samples and the life of the clad material. This is a secondary effect, often marked by the overriding influence of clad-core interface condition. Structures containing some alpha uranium, which disintegrate as bare samples in practically zero time, may show very long clad corrosion lives. Cored structures, compositional homogeneity, aging effects, etc. appear to have little or no effect. Of course large amounts of alpha uranium in the core alloy ruin corrosion resistance.

2. Test temperature. In general, the corrosion life of clad samples shows much the same variation with temperature as the corrosion rate of bare samples.

3. Defect size and shape and clad thickness. These factors, if important at all, are masked in general by other effects.

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FIGURE 1

CORROSION FAILURE OF SIMULATED FUEL ELEMENTS OF
AS-EXTRUDED ZIRCALOY GLAD U-10.5 MO
ALLOY TESTED IN 750°F STEAM

NEG. NO. M1380-3

IX

(A) FUEL RODS AFTER 58 DAYS. PIMPLES NOTED
AFTER 51 DAYS IN TEST.

NEG. NO. 8627A-1

3X NEG. NO. 8549A-1

3X

(B) LONGITUDINAL AND TRANSVERSE VIEW THROUGH
TWO OF THE DRILLED HOLES OF ROD #27.

FIGURE 1 (CON'T)

CORROSION FAILURE OF SIMULATED FUEL ELEMENTS OF
AS-EXTRUDED ZIRCALOY CLAD U-10.5 MO
ALLOY TESTED IN 750°F STEAM

NEG. NO. M1397-2

IX

NEG. NO. M1420-2

IX

(C) AFTER 65 DAYS CRACKING OF CORE ALLOY HAS CAUSED RUPTURE OF #25. GRADUAL CRACKING OF #26 HAS CAUSED STEP-WISE PEELING BACK OF CLADDING OF #26. NOTE CREASES IN OUTER SURFACE OF CLADDING

FIGURE 2
CORROSION PHENOMENA IN CORROSION TESTED ZIRCALOY - CLAD
U-MO ALLOYS

NEG. NO. 6602A-2

400X

(A) TYPICAL MICROSTRUCTURE OF U-MO CORE ALLOY THAT CRACKED DURING CORROSION TESTING. NOTE OXIDE RETAINED IN CRACK (GRAY FINGER, UPPER LEFT CORNER) TERMINATING IN BRANCHING OF OXIDIZED CRACKS, AND HYDRIDE PLATELETS IN UNAFFECTED MATRIX.

NEG. NO. 2482B-1

50X

(B) CROSS SECTION THROUGH 0.040" HOLE DRILLED THROUGH CLADDING
SAMPLE # 206 TESTED 252 DAYS IN 650°F WATER.

FIGURE 3
CORROSION PHENOMENA FOR ZIRCALOY CLAD U-10 NB ALLOY
SAMPLE (#67) TESTED 330 DAYS IN 650°F WATER

NEG. NO. 2496B-3

X 35

(A) CROSS SECTION THROUGH HOLE DEFECT ORIGINALLY DRILLED
ABOUT ONE-HALF THE CLADDING THICKNESS INTO THE CORE ALLOY.

NEG. NO. 2496 B-4

X 250

(B) TRANSFORMATION OF GAMMA PHASE OF HIGHLY CORED URANIUM ALLOY
OF AS-EXTRUDED ELEMENT SHOWN ABOVE.

FIGURE 4
CORROSION AT INTERFACE OF CORE AND CLAD OF EXTRUDED
ELEMENTS

NEG. NO. M1374

2X

(A) U-12 MO CLAD WITH ZIRCALOY AND HEATED 24 HOURS AT 900°C.
NOTE INTERFACE CORROSION AND SWELLING OF CLADDING AT BASE OF
END PLUG.

NEG. NO. M1383-4

2X

(B) SIMILAR ELEMENT NOT HEAT-TREATED DOES NOT SHOW THE
HEAVY GENERAL CORROSION AT INTERFACE. EXTRUSION IS BELIEVED
TO HAVE A REGION OF POOR BONDING NEAR FAILED END.

FIGURE 5
CORROSION FAILURE OF U-10 NB ELEMENT (#327) HEATED 24
HOURS AT 800°C

NEG. NO. 1777 B-3

X35

(A) CROSS SECTION AT HOLE DRILLED JUST THROUGH THE CLADDING .
NOTE ABSENCE OF PIMPLING AT HOLE AND INTERFACE CORROSION
WHICH HAS SEPERATED CORE AND CLADDING.

NEG. NO. 1777 B-4

X250

(B) HYDRIDE PLATELET PRECIPITATION IN URANIUM ALLOY. NOTE ALSO
THE TRANSFORMATION OF GAMMA PHASE TO ALPHA AT GRAIN
BOUNDARIES.

NEG. NO. M1691

IX

(C) ELEMENT FAILED DURING 112-126 DAYS OF TESTING IN 650°F
WATER. INTERFACE CORROSION APPARENT IN CROSS-SECTIONAL
PIECE.

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RECORDED

FIGURE 6

ISOTHERMAL DIFFUSION LAYER GROWTH IN ZIRCALOY-2
FOR URANIUM BASE ALLOYS CLAD WITH ZIRCALOY-2

250 X

(A) U-10 NB: ZIRCALOY-2 COUPLE

250X

(B) U-12 MO: ZIRCALOY-2 COUPLE

FIGURE 7 (CON'T)
INTERDIFFUSION OF CORE AND CLADDING AT 800°C
FOR 24 HOURS

NEG.NO. 8613 A-1

250 X

U: ZIRCONIUM COUPLE

NEG.NO. 8740 A-4

250 X

 U_3Si : ZIRCALOY-2 COUPLE

FIGURE 8
RATE OF DIFFUSION LAYER GROWTH
AS FUNCTION OF TEMPERATURE
FOR U-12 MO: ZIRCALOY-2 COUPLE

FIGURE 9
DIFFUSION LAYERS FORMED DURING EXTRUSION OF U-Mo ALLOYS AT
1040°C

NEG. NO. 8636A-1-1

1000 X

(A) U-9 Mo (EXT. 291-4)

NEG. NO. 8638A-3-1

1000 X

(B) U-12 Mo (EXT. 408-1)

NEG. NO. 8635A-3-1

1000 X

(C) U-13.5 Mo (EXT. 704-6)

FIGURE 10

U-12 Mo : ZIRCALOY-2 DIFFUSION COUPLE

(A) NEG. NO. 1144 B-1-3

250 X

(B) NEG. NO. 1144 B-1-4

500 X

FIGURE II
DIFFUSION LAYER GROWTH AT 900°C FOR
U-12 w/o Mo ALLOYS CLAD WITH ZIRCALOY-2

FIGURE 12

DIFFUSION RESULTING FROM 900°C/24 HOUR ANNEALING IN
U-12 Mo: ZIRCALOY COUPLES WITH Mo AND Ta BARRIER
LAYERS

NEG. NO. 8738A-4-3 100X
(A) APPROXIMATE 0.003" Mo BARRIER WITH TWO DIFFUSION ZONES IN ZIRCALOY.

NEG. NO. 8742A-4-2 250X
(B) APPROXIMATE 0.002" Ta BARRIER SHOWING GAP IN BARRIER. SINGLE
DIFFUSION ZONE IN ZIRCALOY.

FIGURE 13
CORROSION RATES OF ZIRCALOY-2 CLAD URANIUM ALLOY
ELEMENTS IN 650°F WATER AS A FUNCTION OF DIFFUSION
LAYER THICKNESS PRODUCED BY ANNEALING AT 900°C

FIGURE 14

CORROSION FAILURE IN BARRIER LAYER ELEMENTS

CORROSION OF URANIUM ALLOY ADJACENT TO Mo BARRIER IN
ELEMENT ANNEALED 24 HOURS AT 900°C

CORROSION OF URANIUM ALLOY ADJACENT TO Ta BARRIER IN
ELEMENT ANNEALED 24 HOURS AT 900°C. CRACKING OF THE
BARRIER EVIDENTLY RESULTED FROM SWELLING DUE TO CORROSION

88

FIGURE 15

CORROSION LIFE OF U-12 Mo ALLOY VACUUM MELTED IN Mo CRUCIBLE MOLYBDENUM CRUCIBLE SERVED AS BARRIER LAYER DURING EXTRUSION WITH ZIRCALOY-2 CLADDING (EACH BAR INDICATES ONE SAMPLE FROM EXT. #Mo-3A6-6 BLACK INDICATES PERIOD OF FAILURE)

FIGURE 16

CROSS-SECTION THROUGH DRILLED HOLE DEFECT IN ZIRCALOY EXTRUSION-CLAD U-12 MO ALLOY MELTED IN MO CRUCIBLE WHICH SERVES AS BARRIER. ELEMENT #428 HEATED AT 900°C FOR 24 HOURS THEN CORROSION TESTED 126 DAYS IN 650°F WATER

(A) NEG. NO. 2501 B-2

50 X

(B) NEG. NO. 2501 B-11

200 X

90

FIGURE 17
VARIABILITY OF CORROSION LIFE OF ZIRCALOY-CLAD U-9 MO ALLOY
EXTRUDED DIRECTLY TO 0.31" DIA.
(EACH BAR INDICATES ONE SAMPLE.
BLACK INDICATES PERIOD OF FAILURE.)

FIGURE 18

VARIABILITY OF CORROSION LIFE OF ZIRCALOY - CLAD
U-10.5 MO ALLOYS EXTRUDED DIRECTLY TO 0.30" DIA

92

FIGURE 19 (A)
VARIABILITY OF CORROSION LIFE OF ZIRCALOY-CLAD U-12 MO ALLOY
EXTRUDED DIRECTLY TO 0.31" DIA.

FIGURE 19(B)
VARIABILITY OF CORROSION LIFE
OF ZIRCALOY-CLAD U-12 MO ALLOY
EXTRUDED DIRECTLY TO 0.31" DIA.

FIGURE 20

CORROSION FAILURE OF AS-EXTRUDED ZIRCALOY CLAD U-12 Mo ALLOYS
TESTED IN 650° AND 680°F WATER

NEG. NO. MI441-II

IX

- (A) SPLIT IN CLADDING OF #207 OCCURED DURING 42-56 DAY TEST PERIOD
IN 650°F WATER.

NEG. NO. MI420-3

IX

- (B) DISINTEGRATION OF FUEL IN #42 AFTER 76 DAYS OF TEST IN 680°F
WATER.

NEG. NO. MI697

IX

- (C) RUPTURE OF CLADDING OF #59 OCCURED DURING 259-273 DAY TEST PERIOD
IN 650°F WATER.

95

FIGURE 21

CORROSION LIFE OF ZIRCALOY-CLAD U-13.5 MO ALLOY
EXTRUDED DIRECTLY TO 0.31" DIA.

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

96

FIGURE 22

VARIABILITY OF COROSION LIFE ZIRCALOY-CLAD U-10Nb ALLOY EXTRUDED DIRECTLY TO 0.31" DIA.
(EACH BAR INDICATES ONE SAMPLE. BLOCK INDICATES PERIOD OF FAILURE)

FIGURE 23

CORROSION FAILURE OF AS EXTRUDED ZIRCALOY CLAD U-10 Nb ALLOY

- (A) FAILURE OF #64 RESULTING FROM WELD CORROSION DURING 144-158 DAY TEST IN 650°F WATER.

- (B) SEVERE CORROSION FAILURE OF #167 DURING 35-42 DAY TEST IN 750° STEAM.

- (C) SEVERE CORROSION FAILURE OF #168 DURING 28-35 DAY TEST IN 750°F STEAM. NOTE HARD-PACKED OXIDE INITIALLY FORMED IN PIMPLES AT HOLE DEFECTS.

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FIGURE 24A

VARIABILITY OF CORROSION LIFE OF ZIRCALOY-CLAD U-Mo-Nb
TERNARY ALLOYS EXTRUDED DIRECTLY TO 0.5 OR 0.31 DIA.
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD
OF FAILURE)

99

FIGURE 24B

VARIABILITY OF CORROSION LIFE OF ZIRCALOY-CLAD U-Mo-Nb TERNARY ALLOYS
EXTRUDED DIRECTLY TO 0.5 OR 0.31 DIA. (EACH BAR INDICATES
ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

FIGURE 25

CORROSION FAILURE OF EXTRUDED AND HEAT TREATED ZIRCALOY CLAD
 U_3Si_2 ALLOY IN 650°F WATER

NEG. NO. MI724-1

IX

(A) CLAD SPLIT IN 0-7 DAY TEST PERIOD.

NEG. NO. MI420-5

3/4 X

(B) HEAT TREATED CLAD ROD FAILURE IN 0-7 DAY TEST PERIOD.

FIGURE 26

PHOTOMICROGRAPH OF DIFFUSION ZONES IN Zr-U₃Si

102

FIGURE 27

CORROSION LIFE OF ZIRCALOY-GLAD URANIUM ALLOY RODS EXTRUDED DIRECTLY TO
0.31" DIA. AND ANNEALED AT 343°C (650°F) FOR 42 DAYS PRIOR TO EXPOSURE IN
650°F WATER OR 750°F STEAM (1500 PSI)
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

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FIGURE 28

COROSION LIFE OF ZIRCALOY-CLAD URANIUM ALLOY RODS EXTRUDED DIRECTLY TO 0.31" DIA. AND ANNEALED AT 400°C (752°F) FOR 42 DAYS PRIOR TO EXPOSURE IN 650°F WATER
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

FIGURE 29

CORROSION OF BARE SAMPLES OF U-10Nb ALLOY
(EXTR.#405-9) IN 650 °F WATER

FIGURE 30

EFFECT OF ZIRCALOY GLADDING IN EX-
TENDING CORROSION LIFE OF U-12 MO
ALLOYS AS A FUNCTION OF TEMPERATURE

106

FIGURE 31

EFFECT OF TYPE OF DEFECT IN CLADDING OF U-9 MO ALLOY ELEMENT ON CORROSION
LIFE IN 650°F WATER

NEG. NO. M 1064

1 X

- (A) CIRCUMFERENTIAL SLOT 0.7" LONG (LEFT END) LONGITUDINAL SLOT 1.2" LONG (RIGHT END) AND 0.040 DIA. HOLE (MIDDLE OPPOSITE SIDE) ELEMENT AFTER 115 DAYS OF TESTING

NEG. NO. M-1091-1

1 X

- (B) CRACKING OF URANIUM ALLOY RESULTING IN RUPTURE OF CLADDING IN REGION OF LONGITUDINAL SLOT. ELEMENT AFTER 129 DAYS OF TESTING

107

FIGURE 32

EFFECT OF CLADDING THICKNESS ON VARIABILITY OF CORROSION LIFE FOR ZIRCALOY-CLAD
U-12 Mo ALLOY EXTRUDED DIRECTLY TO 0.31" DIA. (MA 303-J680.)

(EACH BAR REPRESENTS ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

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FIGURE 33

EFFECT OF TYPE OF END PLUG ON VARIABILITY OF CORROSION LIFE IN 650°F WATER FOR ZIRCALOY-CLAD U-12 Mo ALLOYS EXTRUDED DIRECTLY TO 0.31" DIA. (EXT. RA49, RA53). (EACH BAR REPRESENTS ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

FIGURE 34

TYPES OF END-PLUGS FOR CLAD URANIUM ALLOY SAMPLES

110

FIGURE 35

CHEMICAL ANALYSIS AND FABRICATION INFORMATION ON DUPLEX MELTED AND EXTRUDED INGOTS

INGOT NO.	EXT. NO.	EXT. TEMP. °F	w/o Mo TOP	w/o Mo BOT.	w/o C TOP	w/o C BOT.	w/o Nb TOP	w/o Nb BOT.	w/o Pt. TOP	w/o Pt BOT.	BARRIER LAYER
J-848-1	M03A1-1	1595	12.0	12.0	.020	.072					NIOBIUM
J843	M03A1-2	1590	10.5	10.6	.014	.018					
J848-2	M03A1-3	1615	12.0	12.0	.020	.072					
J825	M03A1-4	1580	8.0	—	.012	—			1.02	—	
J824	M03A1-5	1610	12.2	12.1	.010	.019			0.51	0.56	
J813	M03A2-1	1590					10.3	—			
J870	M03A2-2	1620			.075	.048	10.6	9.9	1.12	1.59	
J840	M03A2-3	1750			.010	.014	8.3	8.2			
J851	M03A2-4	1750			.018	.020	10.7	10.4			
J852	M03A2-5	1675			.023	.019	10.2	10.1			
J858	M03A2-6	1580	10.5	10.5	.026	.018					PALLADIUM
J915	M03A2-7	1600			.022	.028	12.3	12.0			PLATINUM
J884	M03A2-8	1615	10.5	10.4	.036	.044					
J862	M03A2-9	1580	10.4	10.3	.032	.024					U-15 Mo - 5 Pt
J886	M03A2-10	1580	10.5	10.5	.046	.023					NIOBIUM
J842	M03A2-11	1595			.009	.026	10.5	9.9			MOLYBDEUM
J888	M03A2-12	1610	10.3	10.3	.019	.055					
J892	M03A2-13	1610	10.5	10.5	.033	.062					U-10 Nb

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FIGURE 36

CORROSION LIFE OF ZIRCALOY GLAD U-10.5 Mo DUPLEX
MELTED ALLOY EXTRUDED AND COLD DRAWN ELEMENTS
TESTED IN 650°F WATER. (EACH BAR INDICATES ONE
SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

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FIGURE 37A

CORROSION LIFE OF ZIRCALOY CLAD U-12 MO DUPLEX MELTED ALLOY
EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF
FAILURE)

FIGURE 37B
CORROSION LIFE OF ZIRCALOY CLAD U-12 MO DUPLEX
MELTED ALLOY EXTRUDED AND COLD DRAWN ELEMENTS
TESTED IN 650°F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES
 PERIOD OF FAILURE.)

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FIGURE 38

PROGRESS OF CORROSION ATTACK THROUGH DIFFUSION ZONE IN A BARE END SAMPLE OF U-12 MO ALLOY CLAD WITH ZIRCALOY-2 BY EXTRUSION, COLD DRAWN 48% (R.A.) AND HEATED 24 HOURS AT 900° C. SAMPLE WAS TESTED FOR 7 DAYS IN 650°F WATER. BARE END OF SAMPLE IS BEYOND RIGHT OF PHOTOGRAPH

NEG.NOS. 1710 B1-B2-B3

150 X

FIGURE 39

EFFECT OF HOMOGENIZATION PRIOR TO EXTRUSION
AT 1000°C FOR 48 HOURS

(A) NEG. NO. 2631 B-1

250 X

EXTRUDED WITHOUT PRIOR HOMOGENIZATION

(B) NEG. NO. 845 B-3

250 X

EXTRUDED WITH PRIOR HOMOGENIZATION

116

FIGURE 40 A

EFFECT OF HOMOGENIZATION PRIOR TO EXTRUSION ON THE CORROSION PROPERTIES OF
U-12 Mo DUPLEX MELTED ALLOY CLAD WITH ZIRCALOY-2 IN 650° DEGASSED WATER

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FIGURE 40 B

EFFECT OF HOMOGENIZATION PRIOR TO EXTRUSION ON THE CORROSION PROPERTIES OF
U-12 Mo DUPLEX MELTED ALLOY CLAD WITH ZIRCALOY-2 IN 650°F DEGASSED WATER

118

FIGURE 41A

EFFECT OF ANNEALING ON THE CORROSION PROPERTIES OF 53% COLD DRAWN U-12Mo DEFECTED FUEL ELEMENTS IN 650°F DEGASSED WATER USING INDUCTION CAST AND PRE-HOMOGENIZED FUEL.

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FIGURE 41B

EFFECT OF ANNEALING ON THE CORROSION PROPERTIES OF 53 % COLD DRAWN U-12 Mo DEFECTED FUEL ELEMENTS IN 650°F DEGASSED WATER USING INDUCTION CAST AND PRE-HOMOGENIZED FUEL.

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FIGURE 41C

EFFECT OF ANNEALING ON THE CORROSION PROPERTIES OF 40% COLD DRAWN U-12Mo DEFECTED FUEL ELEMENTS IN 650°F DEGASSED WATER USING INDUCTION CAST AND PRE-HOMOGENIZED FUEL

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FIGURE 42A

EFFECT OF ANNEALING ON THE CORROSION PROPERTIES OF COLD DRAWN U-12
MO DEFECTED FUEL ELEMENTS IN 650°F DEGASSED WATER USING DUPLEX
MELTED AND PREHOMOGENIZED FUEL
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

122

FIGURE 42 B
EFFECT OF ANNEALING ON THE CORROSION PROPERTIES OF COLD DRAWN
U-12 DEFECTED FUEL ELEMENTS IN 650°F DEGASSED WATER USING DU-
PLEX MELTED AND PREHOMOGENIZED FUEL
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

FIGURE 43

DUPLEX MELTED U-12 Mo ALLOY HOMOGENIZED AT 900°C FOR
48 HOURS PRIOR TO EXTRUSION AND COLD DRAWING

NEG. NO. 2283 B-1

250 X

(A) AS EXTRUDED

NEG. NO. 2284 B-1

250 X

(B) 53% COLD DRAWN

NEG. NO. 2291 B-1

250 X

(C) 53% COLD DRAWN +
700°C/5 MIN./W.Q.

FIGURE 44

CORROSION LIFE OF ZIRCALOY CLAD U-8% Nb DUPLEX MELTED ALLOY
EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

FIGURE 45

CORROSION LIFE OF ZIRCALOY CLAD U-10% Nb DUPLEX MELTED ALLOY EXTRUDED ELEMENTS TESTED IN 650°F DEGASSED WATER. (EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

FIGURE 46A

CORROSION LIFE OF ZIRCALOY CLAD U-10 W% Nb DUPLEX
MELTED ALLOY COLD DRAWN ELEMENTS TESTED IN 650°F
DEGASSED WATER
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES
PERIOD OF FAILURE.)

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FIGURE 46 B

CORROSION LIFE OF ZIRCALOY CLAD U-10 W/0 Nb DUPLEX MELTED ALLOY COLD
DRAWN ELEMENTS TESTED IN 650°F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

FIGURE 47

EFFECT OF HEAT TREATMENT AT 900°C FOR 24 HOURS AND CORROSION OF BARE END SAMPLES IN 650°F WATER ON THE DIFFUSION ZONE BETWEEN ZIRCALOY-2 AND U-10%Nb ALLOY

NEG. NO. 1147 B-1-I

100 X

(A) EXTRUDED + 900°C/24 HR/W.Q.

NEG. NO. 1814 B-I

100 X

(B) EXTRUDED + 900°C/24 HR/W.Q. + 21 DAY CORROSION IN 650° F WATER

NEG. NO. 1250 B2-2

100 X

(C) COLD DRAWN + 900°C/24 HR/W.Q.

NEG. NO. 1830 B-I

100 X

(D) COLD DRAWN + 900°C/24 HR/W.Q. 21 DAY CORROSION IN 650° F WATER

FIGURE 48

EFFECT OF CORROSION IN 650°F WATER ON 8% AND 10% Nb
ALLOYS ANNEALED FOR 24 HOURS AT 900°C AND AGED
FOR 5 WEEKS AT 400°C

NEG. NO. 1750 B-1-8 75 X

(A) COLD DRAWN U-10%Nb
AFTER 28 DAYS IN 650°F
WATER

NEG. NO. 2003 B-5 100 X

(B) EXTRUDED U-10%Nb AFTER
56 DAYS IN 650°F WATER

NEG. NO. 2345 B-1 100 X

(C) COLD DRAWN U-8%Nb
AFTER 56 DAYS IN 650°F
WATER

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FIGURE 49A

CORROSION LIFE OF ZIRCALOY CLAD U-12 % Nb DUPLEX MELTED ALLOY
EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER.
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF
FAILURE.)

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FIGURE 49 B

CORROSION LIFE OF ZIRCALOY CLAD U-12 % Nb DUPLEX MELTED ALLOY
EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER. (EACH
BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

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FIGURE 50

EFFECT OF HEAT TREATMENT AND CORROSION ON
THE CORE-CLAD INTERDIFFUSION ZONE AFTER
ANNEALING AT 900°C FOR 24 HOURS ON U-12^W/0Nb
ALLOY

NEG. NO. 1150 B1-2

100 X

(A) COLD DRAWN + 900° C / 24 HR. / W. Q

NEG. NO. 2343 B-2

150 X

(B) AFTER 70 DAYS IN 650° F WATER

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FIGURE 51A

CORROSION LIFE OF ZIRCALOY-CLAD U-8 MO-1PT DUPLEX ALLOY
EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER.

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF
FAILURE.)

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FIGURE 51B
 CORROSION LIFE OF ZIRCALOY-CLAD U-8 MO-1PT DUPLEX
 MELTED ALLOY EXTRUDED AND COLD DRAWN ELEMENTS
 TESTED IN 650°F WATER
 (EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD
 OF FAILURE.)

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FIGURE 52-A

CORROSION LIFE OF ZIRCALOY CLAD U-12 Mo-0.5 Pt DUPLEX MELTED
 ALLOY-EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER
 (EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

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FIGURE 52-B

CORROSION LIFE OF ZIRCALOY CLAD U-12 Mo-0.5 Pt DUPLEX MELTED
ALLOY-EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

100 x

100x

100x

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FIGURE 54

CORROSION LIFE OF ZIRCALOY CLAD U-10 % Nb - 1% PT DUPLEX MELTED ALLOY-EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F DEGASSED WATER. (EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE)

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FIGURE 55A

CORROSION LIFE OF ZIRCALOY CLAD U-10.5 MO DUPLEX MELTED ALLOY WITH A MOLYBDENUM BARRIER LAYER-EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER.

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

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FIGURE 55B

CORROSION LIFE OF ZIRCALOY CLAD U-10.5 MO DUPLEX MELTED ALLOY WITH A MOLYBDENUM BARRIER LAYER - EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER.

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF FAILURE.)

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FIGURE 55 A

CORROSION LIFE OF ZIRCALOY CLAD U-10.5 Mo DUPLEX MELTED
ALLOY WITH A NIOBIUM BARRIER LAYER—EXTRUDED AND COLD
DRAWN ELEMENTS TESTED IN 650° WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD
OF FAILURE.

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FIGURE 56 B

CORROSION LIFE OF ZIRCALOY CLAD 10.5 MO DUPLEX MELTED
ALLOY WITH A NIOBIUM BARRIER LAYER-EXTRUDED AND COLD
DRAWN ELEMENTS TESTED 650° WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES
PERIOD OF FAILURE

FIGURE 57

PATH OF CORROSION ATTACK IN AN EXTRUDED 10.5 MO
ALLOY WITH A NIOBIUM BARRIER AFTER 84-98 DAYS
IN 650°F WATER

(A) NEG. NO. 3185 B-1

250 X

CORE ALLOY AT BOTTOM

(B) NEG. NO. 3186 B-2

250 X

CORE ALLOY AT BOTTOM

FIGURE 58

U-10.5 MO WITH A NIOBIUM BARRIER HEAT TREATED AT 900°C
FOR 24 HOURS AFTER COLD DRAWING (NIOBIUM BARRIER
NON-EXISTENCE AS SUCH AFTER HEAT TREATMENT

NEG. NO. 877 B1-2 250 X

(A) AS HOMOGENIZED

NEG. NO. 1544 B-1-2 7 X

(B) CORROSION TESTED 21 DAYS
IN 650°F WATER - BARE END
ROD

NEG. NO. 1544 B-1-1 250 X

(C) CORROSION TESTED 21 DAYS
IN 650°F WATER - BARE END
ROD

FIGURE 59.

CORROSION LIFE OF ZIRCALOY GLAD U-10.5 M DUPLEX
 MELTED ALLOY WITH A PLATINUM BARRIER LAYER - EXTRUDED
 AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER
 (EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD
 OF FAILURE)

FIGURE 60

CORROSION LIFE OF ZIRCALOY CLAD U-10.5 Mo DUPLEX
MELTED ALLOY WITH A PALLADIUM BARRIER LAYER EXTRUDED
AND COLD DRAWN ELEMENTS TESTED IN 650°F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES
PERIOD OF FAILURE)

FIGURE 61

CORROSION LIFE OF ZIRCALAY GLAD U-105 MO DUPLEX
MELTED ALLOY WITH A U-15 MO-5 PT ALLOY BARRIER
LAYER-EXTRUDED AND COLD DRAWN ELEMENTS TESTED IN
650° F WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES
PERIOD OF FAILURE)

FIGURE 62

CORROSION LIFE OF ZIRCALOY CLAD U-10.5 MO DUPLEX MELTED ALLOY
WITH A U-10% Nb ALLOY BARRIER LAYER EXTRUDED AND COLD
DRAWN ELEMENTS TESTED IN 650°F WATER
(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD
OF FAILURE)

FIGURE 63

GROWTH OF DIFFUSION ZONE AFTER HEAT TREATMENT IN
U-10.5 Mo ALLOY WITH U-10 N_B BARRIER LAYER

NEG. NO. 1767 B-2-1

250 X

(A) 800°C/4 HR/W.Q.

NEG. NO. 1768 B-2-1

250 X

(B) 900°C/10 MIN./W.Q.

NEG. NO. 1150 B-2-2

250 X

(C) 900°C/24 HR/W.Q.

150

FIGURE 64 A

CORROSION LIFE OF ZIRCALOY GLAD U-10% Nb DUPLEX MELTED ALLOY
WITH A NIOBIUM BARRIER LAYER—EXTRUDED AND COLD DRAWN ELEMENTS
TESTED IN 650°F DEGASSED WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF
FAILURE)

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FIGURE 64 B

CORROSION LIFE OF ZIRCALOY CLAD U-10% Nb DUPLEX MELTED ALLOY
WITH A NIOBIUM BARRIER LAYER-EXTRUDED AND COLD DRAWN
ELEMENTS TESTED IN 650° F DEGASSED WATER

(EACH BAR INDICATES ONE SAMPLE. BLACK INDICATES PERIOD OF
FAILURE)

FIGURE 65

EFFECT OF CORROSION ON THE CORE-BARRIER-CLAD
DIFFUSION ZONE AFTER HEAT TREATMENT AT 900°C
FOR 24 HOURS OF A U-10W₀ Nb ALLOY WITH A Nb
BARRIER (BARE END SAMPLE)

(A) NEG. NO. 874 B-1

250 X

ANNEALED 900°C/24 HR/W.Q.

(B) NEG. NO. 2342 B-4

250 X

CORROSION TESTED IN 650°F WATER, FAILED 56-70 DAYS