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OUT-OF-PILE ACCELERATED HYDRIDING OF ZIRCALOY FASTENERS

(LWBR Development Program)

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BETTIS ATOMIC POWER LABORATORY
WEST MIFFLIN, PENNSYLVANIA

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OUT-OF-PILE ACCELERATED HYDRIDING
OF ZIRCALOY FASTENERS

(LWBR Development Program)

J.C. Clayton

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FOREWORD

The Shippingport Atomic Power Station located in Shippingport, Pennsylvania was the first large-scale, central-station nuclear power plant in the United States and the first plant of such size in the world operated solely to produce electric power. This program was started in 1953 to confirm the practical application of nuclear power for large-scale electric power generation. It has provided much of the technology being used for design and operation of the commercial, central-station nuclear power plants now in use.

Subsequent to development and successful operation of the Pressurized Water Reactor in the DOE-owned reactor plant at the Shippingport Atomic Power Station, the Atomic Energy Commission in 1965 undertook a research and development program to design and build a Light Water Breeder Reactor core for operation in the Shippingport Station.

The objective of the Light Water Breeder Reactor (LWBR) program has been to develop a technology that would significantly improve the utilization of the nation's nuclear fuel resources employing the well-established water reactor technology. To achieve this objective, work has been directed toward analysis, design, component tests, and fabrication of a water-cooled, thorium oxide fuel cycle breeder reactor for installation and operation at the Shippingport Station. The LWBR core started operation in the Shippingport Station in the Fall of 1977 and is expected to be operated for about 3 to 4 years. At the end of this period, the core will be removed and the spent fuel shipped to the Naval Reactors Expanded Core Facility for a detailed examination to verify core performance including an evaluation of breeding characteristics.

In 1976, with fabrication of the Shippingport LWBR core nearing completion, the Energy Research and Development Administration established the Advanced Water Breeder Applications (AWBA) program to develop and disseminate technical information which would assist U.S. industry in evaluating the LWBR concept for commercial-scale applications. The program will explore some of the problems that would be faced by industry in adapting technology confirmed in the LWBR program. Information to be developed includes concepts for commercial-scale prebreeder cores which would produce uranium-233 for light water breeder cores while producing electric power, improvements for breeder cores based on the technology developed to fabricate and operate the Shippingport LWBR core, and other information and technology to aid in evaluating commercial-scale application of the LWBR concept.

All three development programs (Pressurized Water Reactor, Light Water Breeder Reactor, and Advanced Water Breeder Applications) have been administered by the Division of Naval Reactors with the goal of developing practical improvements in the utilization of nuclear fuel resources for generation of electrical energy using water-cooled nuclear reactors.

Technical information developed under the Shippingport, LWBR, and AWBA programs has been and will continue to be published in technical memoranda, one of which is this present report.

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Mechanical joints between Zircaloy and nickel-bearing alloys, mainly the Zircaloy-4/Inconel-600 combination, were exposed to water at 450°F and 520°F to study hydriding of Zircaloy in contact with a dissimilar metal. Accelerated hydriding of the Zircaloy occurred at both temperatures. At 450°F the dissolved hydrogen level of the water was over ten times that at 520°F. At 520°F the initially high hydrogen ingress rate decreased rapidly as exposure time increased and was effectively shut off in about 25 days. Severely hydrided Zircaloy components successfully withstood thermal cycling and mechanical testing. Chromium plating of the nickel-bearing parts was found to be an effective and practical barrier in preventing nickel-alloy smearing and accelerated hydriding of Zircaloy.

OUT-OF-PILE ACCELERATED HYDRIDING OF ZIRCALOY FASTENERS

(LWBR Development Program)

J. C. Clayton

I. INTRODUCTION

A. Purpose

The objective of this study was to characterize the extent and effect of nickel alloy-induced hydriding of Zircaloy and to establish the structural stability of certain massively hydrided Zircaloy components. The successful demonstration of chromium-plating as a practical and effective barrier in preventing nickel alloy smearing and accelerated hydriding in Zircaloy components is described also. The information discussed in this report was obtained from work carried out as part of the Light Water Breeder Reactor (LWBR) development program.

B. Background

Most current designs of water-cooled nuclear power reactors contain components made from high-nickel alloys. In certain cases these components are in contact with zirconium alloy components. Typical examples of such high nickel alloy components are, without noting the reactor type specifically, fuel element fasteners, spacer grids, module support plates, wear pads and plenum springs (Reference 1). In addition, nickel-bearing tooling has been used during fuel rod fabrication and module assembly.

Controlled experiments have been previously performed on explosively-bonded Zircaloy-2/Inconel-600 couples in autoclaves and test reactors (References 2 and 3). The results indicated that intimate contact of these dissimilar materials can cause accelerated hydriding in the Zircaloy. Accelerated hydriding is defined as hydrogen pickup from the coolant far in excess of that produced by the $\text{Zr-H}_2\text{O}$ corrosion reaction.

Another investigation found that alloying Zircaloy-2 cladding with 0.2 w/o nickel by eutectic diffusion bonding resulted in high hydrogen ingress rates on exposure to static, degassed neutral water at 680°F (Reference 4). With a hydrogen overpressure of 300 psi above the water saturation pressure, there was extensive hydriding which resulted in Zircaloy disintegration within three days.

Zircaloy components are routinely prefilmed, e.g., oxidized for 3 days in 680°F water, and the resulting oxide acts as a hydrogen barrier between the zirconium and the nickel alloy. Substances such as Neolube, a colloidal suspension of graphite powder in isopropyl alcohol, are sometimes used as lubricants during assembly. However, in certain operations, such as in mechanically attaching a Zircaloy fastener to an Inconel support plate, relative motion (axial, circumferential and radial) can and does occur during assembly. The relative motion is sometimes sufficiently severe and the bearing stress sufficiently high to overcome the protective effects of the corrosion

oxide film and Neolube lubricant. Smearing and bonding of Inconel onto local regions of the mating Zircaloy contact surface occur and provide the potential for accelerated hydriding. Inconel has a relatively high permeability for hydrogen (Reference 2) and acts as a "window" for hydrogen entry into the Zircaloy.

C. Present Study: Scope and Material Properties

This report documents an out-of-pile test program to study hydriding, and determine the strength during thermal cycling and mechanical testing of Zircaloy/nickel-alloy fasteners. Pertinent properties of the test alloys are listed in Table I. Some properties of zirconium hydride and chromium plating also are given in Table I.

Of particular interest for analysis of hydrided Zircaloy/nickel-alloy combinations are tensile properties, coefficient of thermal expansion and density. The delta zirconium hydride phase ($Zr_{H_{1.5}}$) because it has essentially zero ductility and negligible engineering yield strength, ruptures in a brittle fashion under tensile loading. The thermal expansivity of the delta phase is double that of alpha phase Zircaloy-4 and similar to the nickel-alloy values. Thus deformation could occur in the hydrided Zircaloy-4. Density is especially important because the volume of the solid hydride phase is appreciably larger than that of Zircaloy-4. An increase in volume of almost 1 percent occurs for each 1000 ppm increase in hydrogen; this can give rise to dimensional distortion and possible cracking and spalling of the components due to internal stresses.

II. EXPERIMENTAL DETAILS

A. Test Specimen Description

1. Zircaloy Fastener Assemblies (Figure 1)

The majority of the specimens tested were Zircaloy fasteners consisting of a long Zircaloy-4 stem attached to an Inconel-600 support

plate with a Zircaloy-4 nut. The nut has an integral sleeve section which provides axial flexibility in the attachment to permit large deformations due to preloading and to help compensate for the difference in thermal expansion between the Zircaloy and the Inconel.

The fasteners were preloaded at assembly by applying a small torque to the nut after which the nut was tightened a specific number of degrees of rotation. This method of tightening produced a known amount of strain in the fastener since the strain is dependent only on the pitch of the thread and the initial preload. Tightening the nut by a specific rotation eliminated any large variability of load application. Fastener sizes representing small (0.3"), medium (0.6") and large (0.8") diameter assemblies were tested in this study. Calculated room temperature bearing stresses estimates are 80,000 and 87,000 psi for small, 42,000 psi for medium and 34,000 psi for large fastener types. Some typical medium fastener assemblies are illustrated in Figure 1. All the Zircaloy nuts were corrosion-filmed (3 days, 680°F, static water) before assembly. More specific details on the fastener assemblies, including a sketch, are given in Appendix A.

2. Corrosion Control Coupons

The test samples also included sets of three flat Zircaloy-4 corrosion control coupons, about one inch diameter by 0.04 inch thick, which were clamped together after sandwiching between Inconel-600. In each set one coupon was pickled, another was preoxidized (2 days, 750°F, air), and the third was smeared all over its preoxidized surface with an Inconel rod rotating at high speed in a drill press while simultaneously applying a load to the coupon.

The three Zircaloy-4 coupons were tightly sandwiched together by means of a Zircaloy "C" clamp fitted with a load-applying Zircaloy stud such that one surface of each Zircaloy specimen contacted a machined Inconel-600 coupon. In this way the need for Inconel transfer

and bonding, rather than just tight contacting surfaces, could be evaluated to determine whether bonding by severe smearing was necessary for accelerated hydriding.

B. Nickel Alloy Transfer

The electron microprobe, x-ray fluorescence spectrometer, and spark source mass spectrometer were used to analyze the contacting surfaces of the Zircaloy samples for the presence of nickel alloy.

Metallographic examinations were made on three sectioned Zircaloy-4 nuts and one Zircaloy-4 end stem, all of which had been torqued onto Inconel-600 support plates, in order to evaluate the nature of the contact at the Zircaloy/Inconel bearing surface interface.

C. Autoclave Hydriding Tests

1. 450°F

Autoclave hydriding tests were conducted in two phases. For the first phase the test conditions were selected to rapidly develop massive hydriding. This was done by exposing the out-of-pile test specimens to low temperature (450°F) water containing a high level of dissolved hydrogen (620-780 cc H₂/kg H₂O) and a low level of dissolved oxygen (< 20 ppb O₂), while maintaining the pH 10.1 - 10.3 with NH₄OH.

2. 520°F

The autoclave test conditions for the second phase of the hydriding program, except for the absence of neutron and gamma flux, were more representative of pressurized water reactor core operating temperature (520°F), and dissolved hydrogen (50-60 cc H₂/kg H₂O). The oxygen level was kept at < 20 ppb and the pH at 10.1 - 10.3, NH₄OH.

D. Hydride Examination

1. Metallography

The Zircaloy fasteners were disassembled for metallographic inspection by cutting at the nut/end stem location indicated in Figure A-1. This procedure prevented further Inconel transfer had the nut been removed by detorquing.

Each hydrided Zircaloy specimen was mounted transversely with the bearing surface which had been in contact with the nickel alloy material exposed, ground to various depths from the bearing surface, and polished and etched* to reveal hydride at increasing distances from the bearing surface. The first plane examined was located 0.5 to 1 mil below the bearing surface. Based on the hydride concentration and its distribution at this plane, one or more worst case regions were inspected and photographed at various magnifications (10X, 25X, 100X, 500X). Visual estimates of the hydrogen levels in these regions were made by comparison with photomicrographic standards whose hydrogen concentrations had been measured. This procedure was repeated at each grinding level until the hydrogen content dropped below about 500 ppm. Some samples were remounted longitudinally after the first 1 mil grinding operation to reveal the over-all hydrogen distribution.

The first transverse plane examined, i.e. that closest to the bearing surface, was also used to obtain estimates of the percentage of bearing surface occupied by (a) solid hydride and (b) hydrogen contents above about 500 ppm. Planimeter measurements of such areas, combined with visual inspection of 10X photomicrographs of the first and subsequent planes, helped to identify these areas as well as circumferential, radial and axial hydride distribution.

*70 ml. of 30% hydrogen peroxide, 30 ml. of 70% nitric acid, and 5 drops of 48% hydrofluoric acid.

2. Hydrogen Analyses

A manometric vacuum extraction technique was used for measuring the hydrogen content of selected hydrided Zircaloy samples. The procedure consisted of collecting the gases evolved by vacuum extraction at 1300°C, separating hydrogen gas by diffusion through a palladium membrane, and manometrically determining the hydrogen volume.

3. X-Ray Diffraction

The phase compositions in several heavily hydrided Zircaloy nut surfaces were determined by x-ray diffraction. These measurements were supplemented by chemical analyses and metallographic examination on the same specimen.

E. Mechanical Testing of Hydrided Fasteners

1. Thermal Cycling Tests

Selected hydrided Zircaloy fastener assemblies in their as-tightened state were subjected to 30 thermal cycles by being heated in an air furnace between 175 and 550°F with interruption at 10 and 20 cycles for visual examination, and photographing of any observed deformation, spalling or cracking. The heating and cooling rates were about 375°F/hr.

2. Mechanical Tests

Selected hydrided fuel rod fasteners were loaded in tension (nuts in compression) to 166 pounds at room temperature and to 138 pounds at 500°F. A strain gauge was cemented to the outside of each nut near the nut/Inconel bearing surface to record axial strain during successive loading and unloading cycles. Additional hydrided nuts were subjected to room temperature load-deflection test cycles at successively increasing loads. The mechanical load deflection tests

were performed in an Instron machine at a constant heat rate of 0.02 in./minute. The load-deflection curves were autographically recorded.

III. RESULTS AND DISCUSSION

A. Inconel Transfer in Zircaloy/Inconel Fasteners

1. Identification of Inconel Transfer

Representative Zircaloy-4 small and large diameter nuts were examined to determine the extent of transfer of Inconel from the Inconel-600 plate to the contacting surface of the nuts as a consequence of torquing during assembly operations. The electron microprobe, X-ray fluorescence spectrometer, and spark source mass spectrometer were used to analyze the contacting surface of the nuts for the presence of nickel. Except for one unassembled control sample, all specimens were found to have nickel on the contacting surface. Other constituents of Inconel-600 in addition to nickel were detected, thus confirming the transfer to the nuts of Inconel-600 from the plate. Finally, analysis by energy dispersive X-ray spectrometry on some of the nut samples verified that the composition of the transferred Ni-bearing particles on the Zircaloy-4 contact surface was the same as that of an Inconel-600 standard.

As shown in Figure 2, the nickel (Inconel) is distributed non-uniformly over the nut contact surface, in a circular path consistent with the rotary motion during torquing. Macroscopic inspection of the nut surfaces indicated that the relative motion, both rotary and radial, which occurs during torquing and detorquing operations, either partially or completely removes the original corrosion oxide film, scores the underlying Zircaloy and permits direct contact of Inconel. The analytical data, detailed in Appendix B-1, showed that the percentage of the nut bearing surface affected by Inconel-600 transfer was extensive but variable.

2. Measurement of Inconel Transfer and Bonding

Since accelerated hydriding most probably occurs in those regions in which the Inconel is in intimate contact with the Zircaloy, the percentage of bearing surface area having bonded Inconel is of special interest. The nuts are corrosion filmed and then assembled with Neolube lubricant and these materials (i.e., about 0.65 microns of zirconium oxide plus graphite) could act as barriers by reducing the amount of transferred Inconel bonded to the bearing surface. Lack of a metallurgical bond and retention of oxide and/or graphite between the transferred Inconel and the underlying Zircaloy surface might prevent or at least minimize accelerated hydriding despite damage of the corrosion oxide film during fastener assembly operations.

On the other hand, factors which would enhance Inconel transfer and bonding are (a) increasing the number of torque cycles above one (normally used during fastener assembly) and (b) increased radial motion and/or circumferential motion resulting from various degrees of nut misalignment during each preload torquing operation.

Three Zircaloy small diameter nuts were assembled with Neolube and torqued on a Inconel-600 plate as described in Table II. The fasteners were disassembled by cutting to eliminate any additional Inconel transfer during detorquing.

During the torquing operation, the nuts frequently slip radially on the Inconel plate; the amount of slipping observed on the three test samples varied from only a few mils for small diameter nut #41 up to a maximum of approximately 30 mils for the other two nuts. This slippage caused plastic flow of the contacting surface of the nuts and removal of the zirconium oxide film, thus permitting Zircaloy-4 to come into intimate contact with Inconel-600. Metallographic examinations were then made of these nuts in order to evaluate the damage at the bearing surface and the nature of the contact at the Zircaloy/Inconel interface.

The disassembled torqued nuts were mounted longitudinally and were progressively ground through successive planes to view essentially the entire contact surface cross section. The bearing surface was inspected at each stage and photomicrographs were taken to illustrate significant differences in degree and intimacy of contact at the Zircaloy/Inconel interface. Some transferred Inconel was observed on the contacting surfaces of all three nuts. Linear measurements were made from the photomicrographs of the amount of Zircaloy contact surface with a protective ZrO_2 film, the amount of bare surface, and the fraction of surface in contact with the transferred Inconel.

The measurements are discussed in detail in Appendix B-II and the results are summarized in Table II. The observed transferred Inconel was, with few exceptions, a small fraction (≤ 20 percent) of the contact surface and approximately 50 percent of this Inconel was unbonded, i.e., not in intimate contact with the Zircaloy bearing surface. The percent of bearing surface identified with both total transferred Inconel and bonded Inconel was significantly affected by torquing operations, increasing with the number of torque cycles and amount of lateral displacement of the small diameter nut during torquing.

A typical bonded Inconel region was approximately 0.5 mil long and about 0.1 mil thick. The largest bonded Inconel area observed was around 4.5 mils in length; the thickest bonded Inconel was 0.5 mil.

Electron microprobe analyses and metallographic examination also showed some Inconel transfer (approximately 10 percent) on one of the chamfered edges of a Zircaloy 4 end stem. This component, which had been corrosion filmed, was inadvertently misaligned during assembly of a test specimen (a condition not allowed to occur during core fuel rod assembly) and offered an opportunity to find out whether this type of rubbing action was sufficiently severe to remove the ZrO_2 film and allow some transfer and bonding of Inconel to occur.

B. 450°F Autoclave Tests

These tests were performed to rapidly develop massive hydriding in Zircaloy fastener assemblies and subsequently to determine the structural integrity of these hydrided components. An analytical model for hydrogen ingress into nickel alloy-smearred Zircaloy surfaces, described in Appendix G, predicts that the depth of solid hydride rim increases as hydriding temperature decreases, reaches a maximum value and thereafter remains constant. This phenomenon is dependent on the critical value of the hydrogen ingress rate for the test temperature, i.e., if the critical rate is exceeded, solid hydride rimming will occur. Thus a relatively low autoclave test temperature (450°F) and high hydrogen level (520 - 780 cc H₂/kg H₂O) were selected. The oxygen was kept as low as possible (< 20 ppb O₂).

Finally, variables thought to promote accelerated hydriding were exaggerated. Small diameters (0.3") fasteners were tested because of their high bearing stresses (Table A-1). Assembly variables were selected to increase the area of Zircaloy affected by Inconel transfer and bonding. These included: (1) the use of 1, 2 and 3 assembly torque cycles for nuts hydrided assembled, (2) even higher (4 and 6) torque cycles for nuts hydrided disassembled, (3) intentional smearing of the nut bearing surface region with Inconel for some assembled and disassembled nuts, and (4) deletion of Neolube lubricant during assembly of some nuts. An overall view of the significant information on assembly variations and hydriding conditions is presented in Table III. The autoclave exposure time periods were relatively short as no attempt was made to determine if the extent of accelerated hydriding became limiting with time.

1. Hydriding Tests

a. Assembled Fasteners

(1) Single Torque Cycle

Three single-torqued fasteners assembled with Neolube lubricant were examined; two (#6 and #2) after mechanical testing and one (#157) as hydrided. As summarized in Table III, these nuts had the smallest amounts of solid zirconium hydride and high hydrogen (above about 500 ppm). Nut #6 had only small, local solid hydride regions. These were shallow, extending to a depth of only 0.5 mil. No evidence of cracks was noted at the hydrided bearing surface or after skim grinding below this surface (Figure 3). This low degree of hydride involvement was due to the single torque cycle, use of Neolube lubricant and relatively short 4-day exposure time. In addition the slight amount of lateral motion, as evidenced by light scoring of the bearing surface and lack of raised and/or depressed areas (Figure 3A), indicated that the nut was well aligned during assembly. Thus only a minimal amount of Inconel transfer and bonding occurred.

Compared to nut #6, nut #2, with more autoclave exposure time, had a greater solid hydride depth, cracks, and more extensive circumferential involvement of high hydrogen. However, its bearing surface displayed areas of solid hydride and high hydrogen (Table III) similar to nut #6.

Nut #157, with the same assembly conditions and autoclave exposure time as #2, had a greater depth of solid hydride and more area of high hydrogen than nut #2 (Table III).

Nuts #35 and #81, torqued once without Neolube lubricant, had much more hydrogen involvement and greater depths of solid hydride (Table III) than the other nuts torqued once with Neolube lubricant. The axial distribution of hydrogen in 4 of the single-torqued nuts is plotted in Figure 4, and the data indicate that the Neolube lubricant reduces the amount of accelerated hydriding.

(i) Multi-Torqued Cycles

Four double-torqued nuts were hydrided; two (#173 and #163) assembled with and two (#43 and #64) without Neolube lubricant. The hydride examination results were similar to those for single-torqued nuts with respect to the use of Neolube lubricant. In general, greater hydride involvement was noted for the nuts assembled without the Neolube lubricant (Table III). The axial distribution of hydrogen in all 4 double-torqued nuts, plotted in Figure 5, also indicates the beneficial effect of the Neolube lubricant in minimizing accelerated hydriding. The severity of hydriding, cracking and spalling were increased by the double torquing both with and without Neolube lubricant.

Spalling, severe cracking, extensive solid hydride rimming and high hydrogen involvement were found in the triple-torqued nuts #10 and #9 after hydriding and mechanical testing (Table III; Figure 6). The bearing surface of nut #10 has severe and non-uniform scoring (Figure 6A). A lip (or raised region), starting where spalling occurred and extending about 150 degrees of arc, shows that about 20 mils of lateral displacement took place during assembly. This possibly resulted in shearing off part of the lip in the spalled region on retorquing. The appearance of the bearing surface suggests uneven distribution of preload and some cocking of the nut during assembly. Lateral displacement, severe scoring and lip shearing are also present in the bearing surface of nut #9 (Figure 6C).

The extensive hydriding in these nuts can be attributed to the increased number of torque cycles, the use of Neolube lubricant only on the first torque cycle and lateral displacement of the nuts during the torquing operation(s). It also was observed that the axial depths of the local hydride rims were not constant in most of the multi-torqued specimens.

A comparison of the maximum depth of hydride rimming and axial hydrogen distributions in the Neolubed single and multi-torqued small diameter nuts is given in Figure 7. The data demonstrate the large effect which the number of torque cycles has on increasing the axial depth of hydride rim. This results from an increased tendency for Inconel transfer and bonding which increase total hydrogen ingress. The effectiveness of the Neolube lubricant in minimizing accelerated hydriding in the assembled Zircaloy/Inconel fasteners is illustrated in Figure 8. The estimated hydrogen concentrations as a function of distance from the nut bearing surfaces are tabulated in Appendix C.

b. Disassembled Fasteners

Two nuts (L2 and L4), assembled per Table III, were disassembled before being hydrided. They were included in the test primarily to rapidly establish whether or not specimen assembly or hydriding conditions should be modified for assembled nuts to obtain massive hydriding in a short time.

Specimen L2 was torqued and detorqued 4 times; Neolube lubricant was used only on the first cycle. The extensiveness of hydriding became apparent after grinding 1 mil below the bearing surface. Figure 9 is a montage of this surface (reduced in printing from 100X). Essentially the entire surface consists of solid zirconium hydride with only intermittent small areas of alpha plus delta phases. Considerable circumferential cracking is observed with several regions at the external periphery showing hydride spalling. Such cracking and spalling is consistent with the volume expansion and brittleness of the zirconium hydride phase discussed previously (Section I-C). As shown in Table III, solid hydride extended to a depth of about 15 mils. A comparison between nuts L2 and #10, both hydrided for 4 days, is limited by the difference in torque cycles (4 vs 3) and the fact that L2 was not restrained by the compressive preload. Yet, as seen in Figure 7 and Table III, a marked increase in

solid hydride rim depth is observed. This difference in hydride depth (10 vs 15 mils) and surface involvement (22 vs 98%) suggests, however, that the compressive restraint resulting from assembly preloading may be of considerable benefit in restricting cracking and, possibly, reducing depth of hydride rimming and/or surface involvement by decreasing hydrogen diffusion rates into the bearing surface.

Nut L4 received 6 torque cycles before being disassembled and hydrided. Figures 10A and 10B illustrate the resulting hydride. Severe scoring, circumferential cracking and spalling at the bearing surface are evident in Figure 10A. Figure 10B and Table III show essentially 100 percent coverage of the bearing surface by solid hydride and local rimming and cracking beyond 18.8 mils from the surface. These results support the supposition that solid hydride rimming and cracking as well as general hydrogen involvement are strongly affected by the number of torque cycles and the presence or absence of compressive restraints.

Nut N1 was not assembled as part of a fastener. Instead an attempt was made to extend hydride rimming axially by intentional smearing with Inconel. First the Zircaloy-4 nut was rapidly rotated in a drill press while its bearing surface was forced against an Inconel-600 plate. Then, the inner and outer peripheries of the nut were smeared with Inconel-600 for an axial distance of about 0.125 inch by forcing a hand-held Inconel-600 rod against the rotating Zircaloy-4 nut. Figures 10C and 10D show the hydrided nut. The deformation, cracking and spalling at the bearing surface and peripheries are indicative of the severity of the smearing process. Grooves over 5 mils deep were produced at the bearing surface in addition to plastic folds at the outer periphery. Further grinding indicated localized hydride rimming at the inner periphery.

Thus, despite attempts to uniformly transfer Inconel to the Zircaloy specimen peripheries, apparently only local areas were bonded and developed solid zirconium hydride rims. This confirms the

finding of Section III-A which indicates that it is the area of transferred Inconel metallurgically bonded to the Zircaloy that is the controlling factor for accelerated hydriding. Localization of rimming also suggests that the corrosion oxide film is a strong deterrent to Inconel bonding. Even if removed by the severe rubbing action involved in smearing, the oxide film may sufficiently dilute the Inconel/Zircaloy debris so that the portion of the transferred area that becomes bonded to the underlying metal is significantly reduced.

c. Corrosion Control Coupons

Three sets of Zircaloy-4 coupons, tightly clamped together in contact with Inconel-600 coupons as described in Section II-A-2, were autoclaved at 450°F. The details on sample surface and hydriding conditions are given in Table IV. One Inconel-smear coupon (#29), metallographically examined without being autoclaved, showed both bonded and unbonded Inconel areas on its surface (Appendix C).

No evidence of accelerated hydriding was observed in the oxide-filmed Zircaloy coupons. However, as shown in Figure 11, some accelerated hydriding occurred in localized regions of the pickled coupons with 10.1 and 26.7 days autoclave exposure. This could be due to surface scratching caused by relative motion between the Zircaloy and Inconel contacting surfaces during screw-down of the load-applying stud. The pickled coupon with 7.3 days exposure had only normal, i.e., about 25 ppm, hydride. Thus these findings indicate that, for the most part, simple contact under appreciable load between pickled or oxide-filmed Zircaloy-4 and Inconel-600 surfaces resulted in negligible accelerated hydriding.

The results for the Inconel-smear Zircaloy coupons, as expected, did show considerable accelerated hydriding. The accelerated hydriding was localized and variable (Figure 12). All three specimens had local regions of hydride rimming. Some areas had high levels of hydrogen (up to about 10 mils depth) without indication of solid

hydride at the surface. When inspected at high magnifications (500 and 1000X), these regions were generally found associated with surfaces in which the original oxide film was severely deformed and oxide debris was intermixed with smeared Inconel. Regions with little, if any, abnormal hydrogen pickup had the oxide film still present below a thin overlay of Inconel.

Although severe surface deformation accompanied the Inconel smearing action, as seen by surface roughness and edge folds in Figure 12, the variability of hydride indicates that the original oxide film was a strong deterrent to uniform accelerated hydriding over the entire Inconel-smeared Zircaloy surface. Finally factors such as stress did somewhat affect the orientation of the hydride platelets. This is also seen in Figure 12 where the hydride is essentially parallel to the very heavily deformed regions at the coupon edges but inclined at about 45° to the local surface regions where rimming occurred. Further inboard of the rimmed regions and deformed edges, the hydride platelets appear to be more randomly oriented. Zircaloy texture also plays a part in hydride orientation and separation of the texture variables from compressive and tensile stresses is not possible for these specimens.

2. Thermal Cycling Tests

The thermal cycling tests were designed to establish the ability of severely-hydrided Zircaloy-4 small diameter fasteners to withstand thermal transients and fatigue. Table V provides a description of the specimens that were thermally cycled. Each group of assembled hydrided fasteners was given 30 thermal cycles between 175 and 550°F. After each 10 cycle interval, the fasteners were visually examined for any deformation, spalling or cracking. The temperature-time heating, holding and cooling rates for a typical 2 hour cycle are plotted in Figure 13. Some fasteners were intentionally assembled with thin Inconel plates, i.e., no counterbore, to permit easy inspection of the nut/plate bearing surface regions after each 10 thermal cycles.

The results of the thermal cycling tests indicated satisfactory performance of the hydrided fasteners. Despite the severe hydride rimming and hydrogen involvement (described in Section III-B.1 and illustrated in Figure 14 for an Inconel-smeared nut hydrided for 34 days at 450°F) no gross cracking, spalling, or loosening of the fasteners was detected upon periodic visual inspection (30X stereo viewing) and hand manipulation of the assemblies. Although solid hydride and cracks are present in the nut bearing region (Section III-B.1 and Figure 14), the hydrided fasteners successfully withstood repeated thermal transients.

Non-perpendicularity was noted in some of the as-assembled fasteners. In some cases, the nuts were cocked one to two degrees relative to the Inconel plate. The gap, illustrated in Figures 15 through 17, is indicative of non-perpendicularity of nut and plate and explains the local plastic deformation observed in the as-assembled nut. It also confirms the occurrence of lateral motion during assembly and its effect on enhancing hydride rimming (discussed in Section III-B.1) and stem bending during mechanical testing (Section III-B.3).

Figures 15 and 16 (A through F) compare the condition of 17.4 day hydrided fasteners after 10 and 30 thermal cycles. After 10 thermal cycles the amount of deformation progressed around the periphery from about 180 degrees to about 300 degrees. Further thermal cycling, however, did not produce a noticeable change. This is consistent with the differential thermal expansion of hydrided versus unhydrided Zircaloy which would be anticipated to cause deformation during the first thermal cycle only. More significantly, with but one exception, no gross cracking or spalling was observed in the deformed regions of any fastener despite up to 38 days of hydriding and subsequent thermal cycling.

The exception was fastener #70, which was torqued twice on assembly and hydrided for 34 days. As illustrated in Figures 17 and 18, some spalling and cracking, observed in the as-hydrided assembly,

was intensified by the thermal cycling tests. The non-perpendicularity of the assembled fastener is shown in Figure 17A. The severity of hydriding in an Inconel-smeared fastener (A 10) with the same autoclave exposure time is seen in Figure 14. Thus, in this instance, the hydrogen-induced increase in volume, i.e., 1% per 1000 ppm of hydrogen, and increase in thermal expansion coefficient of the delta hydride phase (about double that of Zircaloy) was sufficient to enhance cracking and material loss during thermal cycling.

3. Mechanical Tests

a. Tensile Tests on Fastener Assemblies

Eight assembled fasteners were evaluated for their ability to withstand loading after their nuts were hydrided. Assembly of the Zircaloy rod to the Inconel plate results in tensile and compressive loading of the Zircaloy end stem and nut, respectively. After hydriding (plus thermal cycling for specimens #35 and #43), the fasteners were subjected to additional tensile and compressive stresses. This was done by supporting the Inconel plate in a fixture, schematically illustrated in Figure 19, and pulling the end stem section. The nut remained in compression while under load.

Fasteners #9 and #10 served primarily as advance test specimens to establish acceptability of the test fixture arrangement, strain gauge, and load cell outputs. They also provided significant data on the structural stability of the fasteners hydrided as previously described (Section III-B.1; Table III; Figure 6). These assemblies were first loaded at room temperature to 83 lbs, and then unloaded. The results indicated only elastic strain in the nuts; the post-loading strain recorded reading returned to its original preloading value on unloading. The specimens were removed from the machine and inspected for tightness (manually) and for signs of nut cracking or spalling at the hydrided bearing surface region at magnifications up to 30X. There was no evidence of adverse effects on

structural stability, i.e., no cracking or spalling. The test was repeated with the load increased to 166 lbs. No change in behavior was noted.

Following the successive loadings at room temperature, both specimens were tested at 500° F at applied loads of 69 and 166 lbs. Again, normal behavior was noted, i.e., elastic strains in the nut, no looseness of the connectors, and no visual evidence of cracking or spalling in the hydrided nut bearing surface regions. However, examination of the bearing surfaces, after final loading and disassembly, revealed severe localized cracking and the initiation of spalling, as previously described in Section III-B.1 and shown in Figure 6.

The other six fasteners were tested under more severe room temperature conditions, i.e., at successively higher loadings. The fasteners were periodically removed from the test machine and inspected until sufficient strain had occurred to eliminate the assembly preload so that the nut could be easily removed by hand from the end stem. On reloading, the prior loading was often repeated to check the load-deflection observations. Table VI summarizes the assembly variables, the hydriding conditions, the load-deflection cycles, and the cycles after which inspections were performed.

The load vs strain autographic curves showed relatively linear initial behavior and some deviations from linearity at the very high loadings. The direction of deviation from linearity varied from specimen to specimen and was attributed (confirmed upon examination) to the location of the single strain gauge on the nut with respect to whether the stem was bending away from the gauge (lower rate of compression) or towards the gauge (higher rate of compression). As discussed previously, non-perpendicularity of nut/plate, caused by lateral nut motion during assembly of test specimens, was considered responsible for this.

Tensile loads of 500 lbs were required before elastic deformation caused disengagement of the Zircaloy stem from the Inconel plate without loss of preload. Of particular significance was the finding that for all six specimens the nuts could not be hand loosened, i.e., unthreaded from the stems, until the applied load exceeded 1000 lbs. As shown in Table VI, all nuts remained tight after the 1000 lb load cycle, indicating that there was insufficient plastic deformation to loosen the nut/end stem/support plate components at this applied load. At high load applications the nuts became loose and could be easily unthreaded. This was consistent with indications from strain reading that considerable plastic deformation had occurred. Nut loosening was identified at between 1000 and 1250 lbs load for all test specimens.

The periodic visual inspections after the loading cycles identified in Table VI showed no apparent structural instability, i.e., no gross cracking or spalling at the nut/plate region. On disassembly after tensile testing, a more complete picture of the surface condition was obtained. The results were previously described in Section III-B.1 and are illustrated in Figures 20 and 21 for the fasteners with longer autoclave exposure periods. Despite severe degrees of hydride rimming with local regions of spalling and cracking and extensive hydrogen involvement, the ability of the fasteners to maintain assembly preloads and to withstand applied stresses in excess of 50,000 psi was not impaired.

b. Compression Tests on Tubing Samples

Sections of tubing, 1-inch long, 0.3-inch diameter and 22 mil wall thickness, were intentionally smeared with Inconel-600 on one end. In addition, the inner and outer peripheries of two tubing pieces (T-2 and T-3) were smeared with Inconel-600 for an axial distance of about 0.1 inch. The tubing sections were compressed at room temperature and at 500°F at a strain rate of 1.2 in/in/hr. (machine head speed 0.02"/min.), and 0.2% offset yield strength values were

calculated from the autographically recorded load-deformation curves. The compressive test data, listed in Table VII, are in reasonable agreement with test results on unhydrided Zircaloy-4 tubing (Reference 5).

The appearance of the hydrided, Inconel-smeared tubing surface before and after compression testing is shown in Figure 22. The 4 day hydrided surface had a bulged and cracked region which spalled on compression testing. Analysis of the spalled powder from a 7.3 day hydrided sample (T-2) yielded a hydrogen value of 15,714 ppm ($\text{ZrH}_{1.45}$); hydrogen values for the opposite end were 21, 24 and 25 ppm. The results of X-ray diffraction examination of this and other hydrided samples are discussed below.

4. X-Ray Diffraction Studies

The heavily-hydrided surfaces of 6 Zircaloy-4 samples, described in Table VIII, were examined by X-ray diffraction. The surfaces were shown by diffractograms to consist of two phases: the original alpha-zirconium phase of Zircaloy-4 and the delta hydride phase, with a nominal composition of $\text{ZrH}_{1.5}$. The epsilon hydride phase, ZrH_2 , was specifically looked for but no peaks for it were observed in the diffractograms. It is estimated that this test could detect the epsilon phase if it occupied 5 percent or more of the X-rayed surface.

The identification of the hydride as the delta phase was supported by chemical analyses of flakes of hydride removed from the sample surfaces. These showed an average composition of $\text{ZrH}_{1.44}$, which is close to the range of the delta phase.

The absence of the epsilon phase is also indicated by a metallographic etching study. Mueller (Reference 6) has published a representative selection of photographs of the epsilon hydride phase, both as pure material and in mixtures with the delta phase. The

epsilon phase is characterized by a well-developed lamellar structure, readily visible in polarized light. This characteristic structure was not observed in any of the samples, either after etching with the reagents recommended by Mueller or after using any of the standard Zircaloy-hydride etchants. All of the hydride phase appeared to be in the platelet form characteristic of the delta phase. Not only was the lamellar appearance of the epsilon phase not observed, but there were no metallographic indications of small inclusions of a second phase in the solid hydride rims.

C. 520°F Autoclave Tests

These tests were designed to follow in detail the progress of hydriding in Inconel-smear Zircaloy small diameter fasteners exposed to autoclave conditions which simulated pressurized water reactor core coolant environment. The autoclave temperature was increased to 520°F and the hydrogen level was lowered to 50-60 cc H₂/kg H₂O. The oxygen (<20 ppb) and pH (10.1 - 10.3; NH₄OH) were the same as the 450°F test.

1. Hydriding Tests

a. Assembled Fasteners

(i) Metallographic Examination

Table IX identifies the fastener nuts that were metallographically examined, the number of assembly torque cycles, autoclave exposure times and the resulting hydride conditions. Figures 23 and 24 illustrate the hydrided appearance of representative nuts assembled via two torque cycles.

Greater than normal hydrogen, revealed by the dark region of the transverse sections, was present over 75-100% of the bearing surface for all exposure times. The most severely hydrided region indicates the presence of some solid delta phase hydride

($\text{ZrH}_{1.5}$). This phase is identifiable in the 100X magnification photomicrographs as the more or less continuous light region. These solid hydride regions were always found at the external periphery of the nut and were visually observed to be severely deformed upon fastener assembly. This indicates that these regions were subjected to severe scoring, transfer and bonding of Inconel-600 during the two assembly operations.

Consistent with specimen-to-specimen variability in movement and deformation accompanying fastener assembly, the depth of solid hydride rims observed at the nut periphery (Figures 23 and 24; Table IX) varied from less than 1 to up to 10 mils. The depth did not correlate with exposure time, the thickest solid rim being observed in the specimen exposed 63 days while the thinnest was noted in the specimen exposed 88 days.

Cracks were observed in several of the solid hydride rims. This is noted in Table IX and observable in the transverse sections of Figure 23. While these cracks had significant surface length (5 to 17 mils), they were quite shallow and are not detected in the longitudinal sections about a mil below the bearing surface. Their effects on structural integrity should be negligible based on the satisfactory performance of 520°F hydrided fasteners in thermal cycling tests discussed in Section III-C.2.

Table IX and Figures 23 and 24 show that most of the Zircaloy nut bearing surface area, regardless of 520°F exposure time, developed only diffuse rims.* It is apparent from the transverse

*For this report a diffuse rim is defined as a two phase region, i.e., alpha zirconium plus delta zirconium-hydride ($\text{ZrH}_{1.5}$), in which the density of hydride platelets is high, easily distinguishable metallographically, and associated with a relatively steep hydrogen gradient. The thickness of the diffuse rim is based on an arbitrarily selected lower hydrogen level (unless otherwise indicated) of about 2000 ppm.

sections that the level of hydrogen within one mil of the bearing surface is quite variable and is estimated by comparison with the metallographic photographic standards to vary from about 16,300 ppm (adjacent to the solid $\text{ZrH}_{1.5}$ phase) to as low as a few thousand ppm in other regions of the same sections.

This indicates that the local, bonded Inconel-600 spots, even under the severe scoring conditions represented by fastener assembly using two torque cycles, may be sufficiently small and far apart to cause three dimensional rather than one dimensional diffusion of the incoming hydrogen, preventing solid rim formation. Three dimensional diffusion implies that the critical hydrogen ingress rate, required to form and grow solid hydride rims, is significantly increased when the applied stress is insufficient to cause essentially continuous Zircaloy-4/Inconel-600 bonds.

The metallographic data indicate that the total hydrogen ingress did not appear to increase materially with continued autoclave exposure beyond 34 days. This is seen by a comparison of the most severely hydrided regions illustrated in the longitudinal sections of Figures 23 and 24 with 25 and 26 for nuts torqued once and described below. This finding, which implies that the initially high hydrogen ingress rate decreased, and possibly became negligible, after the first exposure period, is supported by the following:

- (1) The density of hydride platelets in the diffuse hydride rim is similar for fasteners exposed from 63 to 136 days.
- (2) The hydride rims are relatively uniform in depth from internal to external diameter.

- (3) The diffuse rim depths, while varying somewhat, are estimated to be about the same, i.e., 20 to 25 mils, at a hydrogen level of about 2000 ppm determined by comparison with metallographic photographic standards.
- (4) The volume of solid hydride rim is very limited.
- (5) Diffusion beyond the hydrogen solubility limit of about 50 ppm at 520°F occurred, but the total hydrogen content in the first 50 mils from the bearing surface does not appear significantly different for specimens exposed from 63 to 136 days.

Metallographic examination of hydrided single-torqued small diameter nuts supported the indication that the initial high hydrogen ingress rate decreases when exposed to 520°F water simulating core coolant environments. Figures 25 and 26 show the general hydride involvement and the most severely hydrided regions while Table X lists the data obtained from inspection of the sectioned nuts.

While accelerated hydriding was observed over extensive areas of the nut bearing surface, the general severity was less with only one torque than that noted for fasteners assembled using two torque cycles. This was expected in view of reduced deformation, Inconel-600 transfer and bond area noted in Section III-A.2.

Significant findings for single-torqued fasteners may be summarized as follows:

- (1) Accelerated hydride involvement of the nut bearing surface area was similar to that observed for components assembled using two torque cycles.
- (2) Solid hydride rims were observed locally at the external periphery of three of the five nuts examined and are believed to be associated with a combined lateral, rotary and axial movement of test specimens during assembly (as in the case of the test specimens assembled using two torque cycles).
- (3) The solid hydride depth was restricted to 1 to 2 mils or less except for one specimen which showed a very local rim up to about 5 mils deep at the external periphery location.
- (4) A very superficial crack, less than 2 mils deep and about 5 mils long, was observed in the solid hydride in one specimen (Figure 26).
- (5) The diffuse rim depth containing a metallographically estimated hydrogen content of 2000 ppm appeared to be limited to about 10-15 mils in the most severely hydrided regions. This compared with 20-25 mils for the previously described nuts and is consistent with Section III-A-2 data relative to reduced Inconel-600 transfer and bonded areas.
- (6) These data suggest that hydrogen-permeable "windows" on Zircaloy-4 components, caused by

smear and bonded Inconel-600, "heal" on a relatively short exposure during core operation. This is confirmed by quantitative chemical analyses discussed below.

(ii) Chemical Analyses

It was concluded that chemical analyses of hydrogen content vs distance from the bearing surface were necessary to confirm the decrease in hydrogen ingress with time suggested by the metallographic observations. This was especially true because of noted specimen-to-specimen variability, the fact that only the most severely hydrided region was inspected in the longitudinal direction and because hydrogen contents estimated metallographically are very approximate, at best. In view of the importance (to many core designs) placed on the long time structural stability of predictions of hydride rim depth for Zircaloy/nickel-bearing alloy combinations subject to smearing and accelerated hydriding, the possibility that the hydrogen-permeable "windows" might heal was considered to merit close and detailed attention.

Mates of the Zircaloy fasteners, autoclaved from 34 to 136 days simultaneously with those identified in Table IX as being metallographically inspected, were disassembled and chips were machined for chemical analysis. The chips were collected for each increment of 5 or 10 mils from the original bearing surface for a cumulative length of 50 mils. The hydrogen values, considered accurate to $\pm 10\%$, were identified with the corresponding median increment thickness, i.e., 2.5, 7.5, 12.5 mils, etc., for chips removed at 5 mil increments, and 5, 15, 25 mils, etc., for those machined at 10 mil increments.

The hydrogen values, determined by a vacuum extraction technique, were plotted versus the distance from the bearing surface and the best least squares fit curves were drawn through the

data. The procedure is described in Appendix D. The area under each curve, from $X = 0$ to $X = 100$ mils, was measured with a planimeter. This permitted calculating the total hydrogen content, in ppm, for each fastener nut.

The total hydrogen, in ppm, was subsequently converted to $\text{mg H}_2/\text{dm}^2$ of bearing surface area for each specimen and used to graphically portray the hydrogen absorption as a function of autoclave exposure time.

Since the shortest exposure periods for which hydrogen values were obtainable from the available autoclaved specimens were relatively long, i.e., 34 and 63 days for nuts assembled using two and one cycle, respectively, and since the data from these specimens indicated the need for information from shorter exposure specimens, supplementary tests were performed. Available specimens which had not previously been autoclaved, were exposed 2, 7, and 12 days. Some specimens were machined to remove an entire 100 mil long ring for chemical analysis while others were machined incrementally to obtain chips, as before. For the latter, the visually fitted hydrogen concentration-depth profiles were used to guide taking planimetric areas. Planimetric integration minimizes visual errors.

Figures 27 and 28 illustrate the variation of hydrogen with distance for the nuts autoclaved between 34 and 136 days and assembled via two and one torque cycle, respectively. Attention is first directed to Figure 27 since Inconel-600 transfer with smeared and bonded areas is maximized with multi-torque cycle assembly operations. The data for 3 of the 5 specimens, i.e., those autoclaved for the longest periods, are in close agreement and can be represented by one curve. The total hydrogen pickup for these nuts did not change significantly for these exposure periods. However, the 34 day curve falls below and the 63 day curve falls above that representing the longest exposure specimens. It is judged that these differences are associated with specimen-to-specimen variability in the fraction of

Inconel-600 transferred and bonded areas as previously discussed in Sections III-A and III-B. The fact that the 63 day hydrogen concentration values fall above the longer time data tends to support this.

Figure 28 provides additional confirmation. The 63, 88 and 117 day data are in fairly close agreement and are represented by one curve, while a lower curve represents the data for the longest 136 day exposure specimen. Thus, if the Inconel-600 transfer and bonding areas were comparable for all specimens, the longest exposure data would be expected to fall on the same or above data points for specimens autoclaved for less than 136 days.

In general the data in Figures 27 and 28 indicate that "healing" of hydrogen-permeable "windows", created by smeared and bonded Inconel-600 on the corrosion prefilmed Zircaloy-4 nut bearing surface, does occur. The initial high accelerated hydrogen ingress rate essentially shuts off during exposure to pressurized water reactor core temperature (520°F) and coolant chemistry. As previously stated, additional small diameter fastener test specimens were autoclaved and analyzed after relatively short exposure periods to supplement the experimental data and to more precisely determine the effect of autoclave exposure time on healing of hydrogen-permeable "windows".

The total hydrogen absorption values in mg/dm^2 of bearing surface area, including the short exposure samples, are listed in Table X and shown graphically in Figure 29. The significant observations may be summarized as follows:

- (1) The hydrogen-permeable "windows" are definitely healed, i.e., the initially high accelerated hydrogen ingress rate is effectively shut off during exposure at 520°F in pH 10.1 - 10.3 NH_4OH containing hydrogen at 50-60 cc/kg water.

- (2) The time required to completely heal the initial hydrogen-permeable "windows" at 520°F is relatively short, i.e., 20 to 25 days.
- (3) The healing time is essentially the same for small diameter fastener nuts assembled by torquing twice as that for nuts assembled by torquing once.
- (4) The total hydrogen absorption, i.e., the level at which the accelerated hydrogen ingress rate becomes essentially zero, is about 30% higher for Zircaloy nuts assembled by torquing twice vs once.
- (5) The additional short time data listed in Table X and shown in Figure 29 support the previous judgment that the data points (for 34, 63 and 113 days), which do not fall close to the drawn curves, represent specimen-to-specimen scatter.

While the above quantitative findings are specifically associated with assembled small diameter fastener nuts, they are judged qualitatively applicable for Zircaloy-4/nickel-bearing material combinations subject to relative motion and smearing before or during core operation at 520°F in hydrogenated pressurized water reactor coolant chemistry. The level of total hydrogen absorbed may be different for various components depending on the Inconel-600 transfer bonded area. The latter can affect the frequency, size and spacing (or continuity) of local accelerated hydrided regions or spots. Also, another factor, such as the applied stress between mating components, may influence the migration of hydrogen away from the smeared surface. Further, intimate contact of the mating surfaces may limit the accessibility of hydrogen-bearing coolant and thus reduce total

hydrogen absorption. However, it is judged that these effects are of secondary importance since all smeared surfaces did hydride and the accelerated hydrogen ingress did essentially shut off within a relatively short time at 520°F. Thus, it is considered reasonable to assume that the healing of hydrogen-permeable regions caused by smearing of Zircaloy with nickel-bearing materials is generally applicable provided that resmearing is not repeated such that new hydrogen-permeable "windows" are formed.

(iii) Suggested Mechanisms for Healing Hydrogen-Permeable Windows

While the mechanism responsible for healing of hydrogen-permeable "windows" caused by smearing of Zircaloy with the nickel-bearing alloys has not been established, there are several possibilities. The first mechanism is associated with diffusion of oxygen through the surface smeared material to the underlying Zircaloy. This diffusion could result in gradual buildup of a zirconium oxide (ZrO_2) barrier at the Zircaloy surface that would reduce hydrogen absorption to the rate expected from the normal Zr/H_2O corrosion reaction. The rate of film buildup would depend on the rates of diffusion through the various layer materials, i.e., the nickel-bearing surface oxide, the smeared nickel bearing alloy, the several Zirconium/nickel reaction layers, the temperature dependence of these diffusion rates and, further, the thicknesses of the various layers. Attempts to detect such oxide film barriers on hydrided, Inconel-smeared samples by electron microscopic examination were unsuccessful. Another possible healing mechanism, judged to be less probable than that described above, but which may assist in hastening healing, could occur by penetration of the corrosion medium along the edges of small size smeared spots at the Zircaloy/Inconel-600 interface. The typical size of bonded spots (i.e., 0.5 mils long by 0.1 mils wide with 2 to 3 micron thick reaction layers) found on smeared surfaces of small diameter nuts may permit such corrosion penetration. It is estimated that about 5000 days at 520°F would be

required to corrode Zircaloy to a depth of about 0.05 mils, i.e., half the width of a typical smeared and bonded spot. Hence, healing by corrosion of an uncontaminated Zircaloy surface underlying the reaction layers is highly unlikely. However, the corrosion rate of nickel-rich Zr-Ni reaction compounds would be expected to be much higher than that of Zircaloy. Thus, corrosion penetration of very small reaction layers starting at surface edges may reduce the number of "windows" in a relatively short time. Progressive diffusion of oxygen through the same layers also may assist formation of a ZrO_2 barrier layer at the Zircaloy surface below the bonded Inconel-600.

b. Corrosion Control Coupons

Three sets of Zircaloy-4 coupons, tightly clamped together in contact with Inconel-600 coupons as described in Section II-A.2, were autoclaved at 520°F. The details on sample surface and hydriding conditions are given in Table XI.

No evidence of accelerated hydriding was observed in oxide-filmed and pickled Zircaloy coupons in contact with Inconel after autoclaving for 34, 63, and 88 days at 520°F. The coupons had only normal hydride contents. This indicates that simple contact under appreciable load between pickled or oxide-filmed Zircaloy-4 and Inconel-600 surfaces does not result in accelerated hydriding on autoclave exposure at 520°F.

The metallographic examinations of the autoclaved Inconel-smeared Zircaloy coupons, as expected, did show considerable accelerated hydriding. The accelerated hydriding was localized and variable (Figure 30), but less than that observed in the 450°F hydrided coupons. In contrast to the 450°F hydrided coupons, none of the 520°F specimens had any regions of solid hydride rimming. Regions with little, if any, high hydrogen pickup had the oxide film relatively intact. In agreement with the 450°F hydrided coupons, the oxide film acted as a deterrent to uniform accelerated hydriding over the entire Inconel-smeared Zircaloy surface.

2. Thermal Cycling Tests

Thermal cycling tests also were performed on the 520°F hydrided Zircaloy-4 small diameter fasteners. The specimens that were thermally cycled are listed in Table XII. As with the 450°F hydrided samples, each group of assembled hydrided fasteners was given 30 thermal cycles between 175 and 550°F. After each 10 cycle interval the fasteners were visually examined for any deformation, spalling or cracking.

The results of the thermal cycling tests indicated satisfactory performance of the hydrided fasteners. No gross cracking, spalling or loosening of the fasteners was detected. This was as expected since the 520°F hydrided nuts did not have the severe solid hydride rimming, extensive hydrogen involvement or cracks associated with the 450°F hydrided samples. However, non-perpendicularity again was noted in some of the assembled fasteners. Triple-torqued and Inconel-smeared fasteners also successfully withstood the thermal cycling tests.

D. Chromium Barrier Tests

The purpose of these tests was to demonstrate, by autoclave hydriding at both 450 and 520°F, the effectiveness of chromium as a barrier between Zircaloy and mating nickel-bearing alloys.

Previous experimental studies (References 7 and 8) indicate that chromium should be an effective barrier to the accelerated hydriding of Zircaloy. It is thought that, unlike Inconel-600, a chromium oxide film having low hydrogen permeability is formed at relatively low temperatures and in relatively short times. Hard chromium plating also has good wear resistance and can be applied to a base metal or alloy by electroplating at thicknesses sufficient to prevent the chromium being worn away by scoring or abrasion during the fastener assembly operation. The plating procedure is described in Appendix F.

Chromium-plated Inconel-600 and 17 - 4 PH alloys were both evaluated as barrier materials in this investigation. However, attention was focussed primarily on the 17 - 4 PH alloy as the preferred base material for the following reasons (Table I): (1) The 17 - 4 PH alloy is a stronger, age hardenable material (165,000 psi yield strength at an Rc hardness of 35) compared to Inconel-600 (about 45,000 psi at about 87 Rb hardness). Inconel, therefore, is more easily deformed during fastener assembly operations, and is more likely to gall and smear Zircaloy in the event that the chromium plating is locally abraded away. (2) The nominal nickel content of 17 - 4 PH (4.6 w/o) is considerably less than that of Inconel-600 (76 w/o). If hydrogen permeability progressively increases as the nickel content of the smearing material increases, the potential for hydriding would be less for 17 - 4 PH if the chromium plating were locally removed during fastener assembly. (3) The linear coefficient of thermal expansion of 17 - 4 PH between room temperature and core operating temperatures (6.0×10^{-6} in/in/°F) is lower than that of Inconel-600 (7.4×10^{-6} in/in/°F) and closer to that of chromium (3.4×10^{-6} in/in/°F) and Zircaloy (3.6×10^{-6} in/in/°F). Thus there would be less relative motion and tendency for peeling or flaking of chromium from the 17 - 4 PH base material due to thermal cycling.

A series of 30 medium diameter (0.6") fastener assemblies was fabricated in which a metal alloy washer (Inconel-600 or 17 - 4 PH) was placed between each Zircaloy-4 nut and a flat Inconel-600 plate. The Inconel plate was fastened to a removable fixture which supplied the restraining effect of the counterbore in an actual core plate. Some typical medium diameter assemblies are shown in Figure 1 after being corrosion tested for 17 days at 450°F.

To permit a more comprehensive evaluation of the effectiveness of the chromium barrier in preventing accelerated hydriding in the fasteners, several assembly and material variables were investigated. The fasteners were assembled: (1) without an interposed washer, (2) with chromium-plated Inconel-600 washers, (3) with unplated 17 - 4 PH

washers, and (4) with chromium-plated 17 - 4 PH washers. All medium diameter nuts were pre-torqued 15.0 inch-pounds (Table A-1) but the final torque rotations varied between 39 and 174 degrees (Table XIII). Other variables included the deletion of Neolube lubricant during assembly of some fasteners and the use of two torque cycles. Where a nut was torqued twice, it was removed from its end plug before a second torque cycle was applied. The effects of these variables on the severity, i.e., depth and area, of hydriding of the Zircaloy nuts were compared by metallographic inspection after autoclaving.

An overall summary of the medium diameter fastener assembly variables and hydriding conditions is presented in Table XIII. The majority of the assemblies were autoclaved at 450°F in a high hydrogen overpressure (620 - 780 cc H₂/kg of water). Five nuts, after exposure in the assembled state for 17 days at 450°F, were carefully disassembled by machining (to prevent scoring if detorqued) and exposed for an additional 35 days at 520°F and 50 - 60 cc H₂/kg H₂O. A sixth nut (M-30) was also exposed to the latter environment in the disassembled condition without prior exposure at 450°F. The water chemistry for both autoclave tests had a pH range of 10.1 to 10.3 NH₄OH and <20 ppb O₂.

Electron microprobe (EMP) analyses were performed on the bearing surface of several medium diameter nuts to establish whether transfer of washer material occurred. This was done for nuts which were assembled: (1) with chromium-plated Inconel-600 washers, (2) with unplated 17 - 4 PH washers, and (3) with chromium-plated 17 - 4 PH washers. Additional variables included thickness of chromium plating, number of torque assembly cycles and number of degrees of final rotation during assembly. The EMP analyses were performed primarily to evaluate the effectiveness of the chromium plating in preventing washer material transfer. The results also provided an insight into the potential hydriding behavior of the plate/washer combination. With one exception (M-30), these nuts were not subjected to autoclave hydriding, but were disassembled by machining for EMP analysis. For this reason they are not listed in Table XIII.

Finally, to assist in the evaluation of EMP analysis, several washers used in the assembly of medium diameter fasteners or as-plated were examined metallographically. This was done to determine the chromium plating thickness and the effect of the assembly operation on the retention of the chromium plating. Details are given in Appendix F.

1. Nuts Torqued Without a Chromium Barrier

Three fasteners (M-18, X-7 and X-6) were assembled, using Neolube lubricant and one torque cycle, against Inconel-600 or 17 - 4 PH, i.e., with no protective chromium barrier. Final torque rotations were 174° for M-18 and X-7 and 100° for X-6. M-18 and X-7 were intended to serve as a base for comparing smearing and accelerated hydriding due to Zircaloy contamination by Inconel-600 and 17 - 4 PH in the absence of a chromium barrier. The post-test hydride conditions of fasteners X-6 and M-18 were intended to provide a direct comparison of the effect of increasing the preload by increasing the final assembly rotation from 100 to 174 degrees -- both fasteners being assembled directly against Inconel-600 and exposed to the same 450°F hydriding environment.

Visual examination was performed on the disassembled hydrided nuts in order to detect any unusual surface features. The contact surface of M-18 had very minor scoring compared to the other two nuts. The three nuts were mounted transversely, polished and examined for the extent of hydriding. The estimated hydride contents at various depths from the bearing surface are listed in Table XIV and nuts X-6 and X-7 are shown at the one mil depth in Figures 31A and 31B. As was found previously in the 450°F autoclave testing of small diameter fasteners that were torqued directly on Inconel-600 (Section III-B), hydride rimming, solid hydride and cracks can be clearly observed.

Nuts X-6 and X-7 were remounted longitudinally after the first one mil grinding operation. The depths of solid and diffuse hydride are given in Figures 31C and 31D. Both the solid and diffuse hydride depths and cracks are much more extensive in nut X-6, assembled directly against Inconel, compared to X-7, assembled against bare 17 - 4 PH washer -- both fasteners being exposed 17 days in the 450°F environment. The improved hydriding behavior of X-7 is all the more emphasized by the fact that increased smearing and bonding would be expected for this nut since its final torque rotation (174°) was greater than that of X-6 (100°). It is judged that the lower nickel content 17 - 4 PH, i.e., 4.6 w/o vs. 76 w/o for Inconel-600, is responsible for its improved hydriding behavior.

A direct comparison between the degree of hydriding in M-18 and X-6 or X-7 cannot be made because of differences in the assembly procedure. The removable extension fixture was not available when fasteners X-6 and X-7 were assembled. This allowed more lateral motion, slippage and smearing of the nut contact surface by the nickel alloy. Less smearing took place during assembly of M-18. The small degree of distortion for M-18, even with the higher (174°) angle of rotation, resulted from better support during assembly. The relatively shallow depth of solid hydride listed in Table XIV and located at the periphery of M-18, as compared to X-6, is also indicative of the difference in assembly technique.

In summary, the 450°F hydriding behavior of medium diameter nuts torqued directly on nickel-bearing alloys without a chromium barrier was as follows:

- (a) Smearing, bonding and accelerated hydriding did occur, confirming prior observations on small diameter fasteners (Section III-B).
- (b) Smearing by 17 - 4 PH, which is harder and lower in nickel content, resulted in less hydride depth and, probably, less

rim area, in Zircaloy-4 compared to the high nickel-bearing Inconel-600.

- (c) Variability between fastener assembly procedures prevented evaluating the effect of final rotational torque when Zircaloy-4 was assembled directly against Inconel-600.

2. Nuts Torqued with Chromium-Plated Inconel Washers

a. Electron Microprobe Analyses of Unhydrided Specimens

Five medium diameter Zircaloy-4 nuts were torqued with thin (~0.04 mil) chromium-plated metal alloy washers placed between the nut and an Inconel-600 plate. Four of the washers were Inconel-600 and the fifth washer was 304 stainless steel. Pertinent assembly data and electron microprobe analyses are described in detail in Appendix E.

The electron microprobe findings on the disassembled unhydrided nuts indicated the following:

- (1) The thin chromium plating did not completely prevent transfer of nickel-bearing washer material to the Zircaloy nut bearing surface.
- (2) The chromium plating, despite its thinness, significantly reduced the area of Inconel transfer compared to that previously observed on nuts torqued without Cr-plated washers (Section III-A; Appendix B).
- (3) The benefits from the thin chromium plating applied for a high final torque rotation (174°) and for both one and two torque assembly cycles.

- (4) In agreement with previous observations (Figures 4 and 8), Neolube lubrication during fastener assembly tended to reduce Inconel transfer.

b. Metallographic Evaluation of Hydrided Specimens

Four medium diameter fasteners were torqued to final rotation angles of 174° , without Neolube lubricant, against thin (~ 0.04 mil) Cr-plated Inconel-600 washers. The assemblies were autoclaved at 450°F at progressively increasing times from 7 to 34 days.

The nuts were mounted transversely and examined for accelerated hydriding. The estimated hydride contents at various depths from the bearing surface are listed in Table XV, and illustrated for the one mil grinding depth in Figure 32. In all cases there was a marked reduction in area displaying solid hydride compared to fastener nuts torqued without a chromium barrier and subjected to the same hydriding temperature and environment.

Estimates of the hydrogen concentration as a function of grinding depth, taken from Table XV, are shown plotted in Figure 33. Two nuts (M-2 and M-3) had only spots of localized diffuse hydride while nuts M-1 and M-4 had some solid hydride with depths of 1 and 3 mils, respectively. Significantly more scoring and gouging were noted on the bearing surface of M-4 and some local cracking occurred near the bearing surface and within the solid hydride (Figure 32D).

Metallographic evaluation of the chromium plating on the four Inconel washers showed that the plating was thicker (~ 0.2 mil) at the washer periphery, but much thinner (~ 0.04 mil) on the contact surfaces. These washers were plated in the same batch and were representative of those used for electron microprobe analyses (Section

III-D.2A; Appendix E). For the two washers torqued with the fasteners which resulted in only small spots of diffuse hydride (M-2 and M-3), the chromium coating remained relatively intact as indicated in Figures 34B and 34C. However, localized coating disruption and loss of coating integrity (Figures 34A and 34D) were observed in the washers associated with the more extensively hydrided nuts (M-1 and M-4).

The hydriding results confirmed the electron microprobe analyses. The chromium plating was too thin to completely prevent accelerated hydriding but drastically minimized the affected area. This was true despite using a high final rotation torque of 174 degrees and despite the lack of Neolube lubrication during assembly. However, no abnormal hydriding occurred where the thin chromium plating maintained its integrity. The findings imply that a somewhat thicker chromium plating is needed to completely avoid accelerated hydriding.

3. Nuts Torqued with 17 - 4 PH Washers

a. Electron Microprobe Analyses of Unhydrided Specimens

Four medium diameter Zircaloy-4 nuts were torqued once, one against a bare 17 - 4 PH washer and three others against Cr-plated 17 - 4 PH washers. Pertinent assembly data and electron microprobe analyses are described in detail in Appendix E.

The electron microprobe findings on the disassembled unhydrided nuts indicated the following:

- (1) Chromium-plated (0.08 - 0.25 mil thick) 17 - 4 PH washers were effective in preventing transfer and smearing of 17 - 4 PH to the Zircaloy nut bearing surface when Neolube lubrication and a 100 degree final rotation were employed.

- (2) Some chromium was transferred to the Zircaloy nut bearing surface during the fastener assembly operation. However, no zirconium oxide film removal or contamination of the Zircaloy substrate with 17 - 4 PH was detected.
- (3) The ZrO_2 oxide film and the use of Neolube lubricant provides added protection against transfer and contamination of Zircaloy by 17 - 4 PH.
- (4) Reducing the final rotation from 174 to 100 degrees does not prevent transfer of unplated 17 - 4 PH washer material to the Zircaloy-4.
- (5) Care must be taken during assembly operations to prevent contact and smearing of Zircaloy surfaces by stainless steel tools, even though this alloy is relatively hard and has a low nickel content.

b. Metallographic Evaluation of Double-Torqued Hydrided Specimens

Three medium diameter nuts (X-19, M-23 and X-8) were assembled using two torque cycles, Neolube lubricant and a final rotation of 100 degrees. Specimen X-19 was assembled with an unplated 17 - 4 PH washer while M-23 and X-8 were torqued on chromium-plated washers having chromium thicknesses of 0.2 and 0.3 mil, respectively. Fasteners X-19 and M-23 were autoclaved for the same 17 day time period at 450°F while X-8 was autoclaved twice as long in the same environment. These specimens provide a direct comparison of hydriding behavior for plated and unplated washer variables subjected to two assembly torquing operations with a high potential for abrasion and removal of the chromium plating.

The contact surface of nut X-19 had very minor scoring compared to the other two nuts. The results of metallographic examination are given in Table XVI. Nut X-19, despite being assembled twice on a bare 17 - 4 PH washer, showed no accelerated hydriding (Figure 35A). The hydride platelets indicate a hydrogen content of less than 50 ppm.

Nut M-23 also showed no accelerated hydriding (Figure 35B). This was expected since the washer was chromium-plated. On the other hand, nut X-8, despite being assembled with a 0.3 mil thick Cr-plated washer, does show some abnormally high hydrogen in local score marks about midway between the I.D. and O.D. at the 2 and 9 o'clock positions (Figure 35C).

The variability in hydriding behavior of the three specimens prevents drawing firm conclusions as to the reason for lack of accelerated hydriding in nut X-19, assembled with a bare 17 - 4 PH washer, and the local hydriding in nut X-8, assembled with a Cr-plated washer. The EMP data (Section III-D.3a; Appendix E) indicate that, in the case of X-19, transfer of 17 - 4 PH material to the Zircaloy nut bearing surface probably occurred during the two cycle torquing operations but the 17 - 4 PH did not bond to the Zircaloy, a condition needed to promote accelerated hydriding. Possibly the ZrO_2 film or debris from wear areas, along with the high hardness of aged 17 - 4 PH, may have helped prevent bonding. For nut X-8, local severe scoring during the two cycle operation apparently caused local removal of ZrO_2 and very restricted transfer and bonding of 17 - 4 PH, resulting in the observed diffuse hydride regions (Figure 35C; Table XVI). Perhaps a local high spot on either the nut or washer bearing surface was the cause. In any case, the local degree of hydriding and diffuse nature of the hydride should not affect structural stability, loss of preload or normal performance of the fastener.

Nuts X-20 and M-24 were also assembled with two torque cycles, Neolube lubricant and a final rotation cycle of ~100

degrees. Specimen X-20 was assembled with a bare 17 - 4 PH washer and M-24 was torqued on a 0.2 mil thick Cr-plated washer. These fasteners were intended to provide additional information resulting from autoclave exposure of 17 days at 450°F followed by continued exposure for an additional 35 days at 520°F. For the latter exposure, the nuts were disassembled without detorquing, i.e., by cutting, to prevent bearing surface damage.

The nuts were metallographically evaluated after the total cumulative exposure of 52 days with results listed in Table XVI. No accelerated hydriding occurred in nut M-24 assembled with a Cr-plated washer but accelerated hydriding did occur in a local region of nut X-20. Figure 35D illustrates the area and severity of hydriding 1 mil below the bearing surface. No solid hydride was observed, but a diffuse region, maximum level 6000 ppm hydrogen and about 180 mils long by about 30 mils at the maximum width, was noted at this depth. The hydrogen content decreased to about 200 ppm at 16 mils below the surface (Table XVI).

The hydriding behavior of fasteners X-20 and M-24 followed the expected pattern. Smearing, bonding and accelerated hydriding, although in a very local region and of a relatively minor nature with no solid but only diffuse hydride, occurred with a bare 17 - 4 PH washer and two torque cycles. Chromium plating the washer to 0.2 mil prevented accelerated hydriding completely despite the two cycle torque assembly operation. An analytical model for the kinetics of hydrogen ingress into nickel-smear Zircaloy surfaces (Appendix G) predicts more hydride rimming at lower temperatures, even though the growth rate decreases with temperature. Because of the higher hydrogen content in the environment in addition to the lower temperature, it is judged that all or most of the hydriding in nut X-20 occurred at 450°F.

c. Metallographic Evaluation of Single-Torqued Hydrided Specimens

Seven medium diameter nuts were assembled using one torque cycle, Neolube lubricant and final rotation of 100 degrees. All specimens were torqued with Cr-plated 17 - 4 PH washers. Several different lots of plated chromium washers (0.2 to 0.45 mil thick chromium) were tested. Six assembled fasteners were autoclaved for the same 17 day time period at 450°F while specimen X-5 was autoclaved twice as long in the same environment. Three nuts, after exposure in the assembled state for 17 days at 450°F, were carefully disassembled by cutting and exposed for an additional 35 days at 520°F.

The results of metallographic hydride evaluation are summarized in Table XVII. No hydride rimming, localized or abnormal hydriding was observed in any of the nuts which were torqued once with Neolubed Cr-plated 17 - 4 PH washers. The hydrogen contents were uniformly distributed and are estimated to be less than 50 ppm. The few scattered hydride platelets at 300X magnification were similar to those shown in Figures 35A and 35B.

These results demonstrate that chromium-plated 17 - 4 PH washers are effective in completely preventing accelerated hydriding in Zircaloy medium diameter fasteners when assembled using one torque cycle, Neolube lubricant, a final rotation of 100 degrees and a chromium plating thickness of ≥ 0.2 mils. Further, the findings indicate that the chromium barrier prevents accelerated hydriding at the core operating temperature of 520°F as well as at the lower 450°F temperature in a high hydrogen water environment.

A final specimen, M-30, was included in the autoclave testing. Nut M-30 was assembled against a bare 17 - 4 PH washer using one torque cycle, Neolube lubricant and a final rotation of 100 degrees. The nut was disassembled by cutting and its contact surface examined by EMP techniques (Appendix E). The nut had several relatively deep, spiral gouges on its bearing surface where the EMP analyses detected 17 - 4 PH transfer. The disassembled nut was then autoclaved for 35 days at 520°F. The metallographic inspection results

are given in Table XVII. Despite the EMP-detected transfer of 17 - 4 PH, no accelerated hydriding was observed. The microstructure showed that the hydride platelets at 1 mil below the bearing surface were uniformly distributed. The hydrogen content was estimated at less than 50 ppm. This test is a relatively close simulation of hydriding that might be expected at 520°F if appreciable scoring and flaking of chromium plating should occur during fastener assembly.

d. Comparison of Hydriding in Specimens Torqued Against Unplated
17 - 4 PH

Because of the variability of the hydriding behavior of the medium diameter nuts torqued against bare 17 - 4 PH washers, these specimens are grouped in Table XVIII in order to compare their differences. Both M-30 and X-7 were assembled using one torque cycle and Neolube lubricant. No accelerated hydriding was observed for M-30 despite transfer of 17 - 4 PH determined by EMP analyses. Nut X-7 displayed considerable hydriding, including solid hydride rimming. However, X-7 was torqued to 174 degrees and autoclaved at 450°F, while M-30 was torqued to 100 degrees and autoclaved at 520°F. Thus a reduction in severity of smearing with the lower angle of rotation and a diminishing of hydrogen ingress due to the lower hydrogen content in the environment and the higher exposure temperature combined to eliminate accelerated hydriding in nut M-30.

Specimens X-19 and X-20 were both torqued two cycles using Neolube lubricant and a final rotation angle of 94 degrees and both were autoclaved for 17 days at 450°F. Nut X-19 had no accelerated hydriding while X-20 showed very local, diffuse hydriding. Variability in similarly-assembled test specimens has been noted throughout this report. Double operations such as torquing, detorquing and repetition of this fastener assembly procedure increase the potential for local smearing, bonding and sample variability.

IV. SUMMARY OF RESULTS

A. Inconel Transfer and Bonding

1. Electron microprobe, X-ray fluorescence and spark source mass spectrometric analysis of bearing surfaces on unhydrided, disassembled Zircaloy nuts showed non-uniform, extensive, but variable, transfer of Inconel from the support plate.
2. Examination of the nut surfaces revealed that relative motion during the torquing and detorquing operations can partially remove the protective oxide corrosion film, score the underlying Zircaloy and permit direct, intimate contact of Inconel.
3. Some transferred Inconel was observed on the contacting surfaces of three disassembled Zircaloy-4 small diameter nuts examined metallographically. The observed transferred Inconel was a small fraction (≤ 20 percent) of the contact surface and approximately 50 percent of this Inconel was unbonded.
4. The percentage of bearing surface identified with both total transferred and bonded Inconel was significantly affected by the torquing operations, increasing with the number of torque cycles and the amount of lateral displacement of the nut during torquing.

B. 450°F Autoclave Tests

1. Hydriding Tests

- a. Accelerated hydriding, particularly solid hydride rimming and cracking, of Zircaloy small diameter nuts varied over a wide range and depended primarily on the

number of torque cycles used during assembly, and whether or not the nuts were hydrided in the assembled or disassembled condition.

- b. The number of preload torque cycles had a large adverse effect on the extent of hydriding.
- c. Use of graphite lubricant reduced the potential for hydride rimming.
- d. Simple contact under appreciable load between pickled or oxide-filmed Zircaloy-4 and Inconel-600 coupon surfaces resulted in negligible accelerated hydriding.

2. Thermal Cycling Tests

No loosening, cracking or spalling was observed for small diameter specimen fasteners thermally cycled 30 times between 175 and 550°F after hydriding 7.3 - 38 days at 450°F.

3. Mechanical Tests

- a. Two small diameter fasteners were tested at room temperature and at 500°F to stresses of 8300 and 6900 psi, respectively. No evidence of loss of preload, spalling or cracking was noted. These specimens had been torqued 3 times, autoclaved for 4 and 11.3 days at 450°F and had developed local regions of solid hydride over 11 to 22% of the nut bearing surface to a depth of up to 10 mils.
- b. Additional fasteners were subjected to room temperature load-deflection tests at successively increasing loads. Tensile stresses of 25,000 psi were required before elastic deformation caused disengagement of the

stem from the base plate without loss of preload. Reproducible results were obtained on six fasteners with nuts hydrided to depths over 10 mils for a bearing surface coverage over 90%.

- c. Tensile stresses between 50,000 and 62,500 psi were required before plastic deformation at room temperature was sufficiently high to cause permanent loosening of hydrided fasteners. No gross cracking or spalling of nuts occurred at these loads. The nuts had been autoclaved for 4 - 21.4 days at 450°F.

C. 520°F Autoclave Tests

1. Hydriding Tests

- a. Accelerated hydriding of Zircaloy small diameter fasteners occurred, but the initial high hydrogen ingress rate decreased rapidly as exposure time increased and was effectively shut off in about 25 days.
- b. The time required to heal the initially hydrogen-permeable windows was not affected materially by the severity of smearing.
- c. The total hydrogen absorbed due to accelerated hydriding, including solid hydride rimming, increased with the severity of smearing.
- d. Simple contact under appreciable load between pickled or oxide-filmed Zircaloy-4 and Inconel-600 coupon surfaces did not result in any accelerated hydriding.

2. Thermal Cycling Tests

No loosening, cracking or spalling was observed for small diameter test specimen fasteners thermally cycled 30 times between 175 and 550°F after hydriding 34, 63, 88 and 117 days at 520°F.

D. Chromium Barrier Tests

1. Chromium-plated (0.2 - 0.45 mil thick) 17 - 4 PH washers, interposed between Zircaloy-4 medium diameter nuts and an Inconel-600 plate, were effective in preventing smearing by nickel-bearing alloys during Neolube-assisted assembly and subsequent accelerated hydriding of the nuts. This was demonstrated by autoclave testing at both 450 and 520°F.
2. Thin (<0.1 mil thick) chromium plating was insufficient to completely avoid smearing by nickel-bearing alloys and thus some subsequent accelerated hydriding occurred at 450°F. However, even a thin chromium plated layer greatly reduced the severity (area and depth) of accelerated hydriding.
3. Autoclave test results on medium diameter fasteners torqued directly on nickel-bearing alloys confirmed the tests on small diameter fasteners in showing that nickel, smeared and bonded onto the bearing surfaces of the Zircaloy-4 nuts during fastener assembly, can result in subsequent accelerated hydriding.

V. CONCLUSIONS

- A. Nickel-alloy smearing and bonding to filmed Zircaloy, rather than just tight surface contact, is necessary for accelerated hydriding.
- B. Heavily-hydrided Zircaloy-4 small diameter fasteners withstood mechanical and thermal cycling tests with no evidence of material spalling, gross cracking or loosening of the fastener components.

- C. The finding that hydrogen-permeable windows in small diameter fastener nuts heal at 520°F after relatively short exposure in pressurized water reactor core coolant chemistry is judged to be qualitatively applicable to similar Zircaloy/nickel alloy combinations subject to smearing during manufacture or core assembly.
- D. Chromium has been demonstrated to be an effective and practical barrier between Zircaloy and mating nickel-bearing alloys.
- E. Direct metal-to-metal contact between Zircaloy and high-nickel alloys should be minimized in water-cooled nuclear power reactors, especially where relative motion can occur between the components.

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REFERENCES

1. M.R. Warren, K. Roerbo and E. Adolph, "Incompatibility between Zircaloy-2 and Inconel X-750 during Temperature Transients", J. Nucl. Mater., 58 185-8 (1975).
2. A.B. Johnson, Jr., "A Review of Corrosion Phenomena on Zirconium Alloys, Niobium, Titanium, Inconel, Stainless Steel and Nickel Plate under Irradiation," Rev. Coatings Corrosion, 1, 299-365 (1975).
3. A.B. Johnson, Jr., "Aqueous Corrosion and Hydriding of Zirconium Alloys in Nuclear Reactor Environments," Proceed. 4th Int. Cong. on Metall. Corr., Amsterdam 1969, pps 168-77, NACE, Houston, Texas (1972).
4. R.A. Wolfe, F.O. Bingman, R.L. Fischer, R.C. LaCerte, E.F. Losco, "Eutectic - Diffusion Bonding of Plate - Type Fuel Elements Containing Ceramic Fuel", WAPD-211 (October 1960).
5. C.R. Woods, "Properties of Zircaloy-4 Tubing", WAPD-TM-585 (December 1966).
6. W.M. Mueller, J.P. Blackledge and G.G. Libowitz, "Metal Hydrides", Academic Press, NY, 1968, pp 275-76.
7. F.W. Pement, "Hydrogen Accumulation Rates Within Thick-Walled Tubes of Fe-Cr and Fe-Cr-Ni Alloys During Exposure to High-pH, High Temperature, Pressurized Water Containing Dissolved Hydrogen", WERL-1114-3 (June 1967).
8. E.A. Gulbransen, K.F. Andrew, S.A. Jansson and A.R. Pebler, "Hydrogen Reactions with Alloys of Zr and the Metals V, Cr, Fe, Co, Ni, Cu, Mo, Nb and Sn," WERL-3203-10 (June 1, 1967).

TABLE I
Test Materials Room Temperature Properties

<u>Material</u>	<u>Inconel-600</u>	<u>17 - 4 PH</u>	<u>Zircaloy-4</u>	<u>Delta - Zirconium Hydride</u>	<u>Chromium Plating</u>
Composition	76 w/o Ni, 16 w/o Cr, 8 w/o Fe	4.6 w/o Ni, 16.7 w/o Cr, 3.5 w/o Cu, balance Fe	1.5 w/o Sn, 0.2 w/o Fe, 0.1 w/o Cr, balance Zr	ZrH _{1.5}	Cr
Thermal Expansion (in/in/°F)	7.4 x 10 ⁻⁶	6.0 x 10 ⁻⁶	3.6 x 10 ⁻⁶	7.9 x 10 ⁻⁶	3.4 x 10 ⁻⁶
Yield Strength (psi)	45,000	165,000	65,000	9000*	70,000
Rockwell Hardness	Rb 87	Rc 35	Rb 90	----	Rc 38
Density (lbs/in ³)	0.304	0.281	0.236	0.204	0.260

*Ultimate tensile strength

TABLE II
Inconel Transfer and Bonding Measurements

<u>Small Diameter Nut Identity</u>	<u>Torque Cycles</u>	<u>Lateral Slippage (mils)</u>	<u>% With Transferred Inconel</u>		<u>% With Bonded Inconel</u>	
			<u>Average</u>	<u>95% Confidence Limits</u>	<u>Average</u>	<u>95% Confidence Limits</u>
Short Length nut 41	1	about 2	3.82	1.23-7.84	1.94	0.58-4.11
Short Length nut 33	1	30	8.53	4.30-14.18	4.10	1.93-7.07
Short Length nut 5	3*	30	15.46	9.52-22.82	8.43	5.5-12.52

*Assembled with Neolube prior to first cycle only.

TABLE III
Hydriding of Small Diameter Fasteners at 450°F

Fastener Assembly Variables				Hydriding Conditions		Post - Hydriding Evaluation				Reference Figure
Fastener Identity	Neolube	Torque Cycles	Final Rotation (Degrees)	Fastener Exposed Assembled	Exposure Time (Days)	Solid Hydride		Cracks	High (>500 ppm) Hydrogen (Area %)	
						Area %	Depth (mils)			
#6*	1	1	60	Yes	4	1	0.5	No	12	3
#2*	1	1	60	Yes	11.3	4	1.4	Yes	11	4
#157	1	1	55	Yes	10.1	4	9.1	Yes	24	-
#35**	0	1	55	Yes	7.3	20	3.7	Yes	65	4
#81	0	1	55	Yes	10.1	60	7.9	Yes	100	4
#173	2	2	55	Yes	10.1	16	8.0	Yes	41	5
#163	1	2	55	Yes	10.1	11	8.8	Yes	49	5
#43**	0	2	55	Yes	7.3	80	8.2	Yes	100	5
#64	0	2	55	Yes	17.4	90	19.2	Yes	100	5
#10*	1	3	55	Yes	4	22	9.6	Yes	90	6
#9*	1	3	55	Yes	11.3	11	9.9	Yes	82	6
L2	1	4	55	No	4	98	14.6	Yes	100	9
L4	1	6	55	No	7.3	100	≥18.8	Yes	100	10
N1	0	0	Inconel	No	7.3	100	10	Yes	100	10

*Hydrided and mechanically tested

**Hydrided, thermal cycled, and mechanically tested

TABLE IV
Autoclaving of Corrosion Control Coupons at 450°F

Identity	Surface Condition	Autoclave Exposure Time (Days)	Post - Hydride Evaluation			Figure Reference Number
			Accelerated Hydriding	Solid Hydrides	Solid Hydride Depth (mils)	
#29	Inconel-Smeared	0	-----	-----	-----	C-1
#1	Pickled	7.3	No	No	-----	-----
#10	Air-Oxidized*	7.3	No	No	-----	-----
#11	Oxidized* and Inconel-Smeared	7.3	Yes	Yes	5-6	12
#2	Pickled	10.1	Yes	No	-----	11
#12	Air-Oxidized*	10.1	No	No	-----	-----
#13	Oxidized* and Inconel-Smeared	10.1	Yes	Yes	4-5	12
#3	Pickled	26.7	Yes	No	-----	11
#14	Air-Oxidized*	26.7	No	No	-----	-----
#15	Oxidized* and Inconel-Smeared	26.7	Yes	Yes	6-7	C-2

*2 days at 750°F

TABLE V
Small Diameter Fasteners for Thermal Cycling Tests

<u>Fastener Identity</u>	<u>Torque Cycles</u>	<u>Counterbore in Inconel Plate</u>	<u>450°F Autoclave Exposure Time (Days)</u>
#35	1	No	7.3
#43	2	No	7.3
A2*	1	Yes	7.3
A3*	1	Yes	7.3
#25	1	No	17.4
#26	1	No	17.4
A4*	1	Yes	17.4
A5*	1	Yes	17.4
#36	1	No	34
#70	2	No	34
A8*	1	Yes	34
A9*	1	Yes	34
#7	3	No	38

*Bearing surface intentionally smeared with Inconel-600 prior to fastener assembly.

All fasteners were assembled without the use of Neolube lubricant.

TABLE VI
Load Deflection Cycles for Room - Temperature Mechanically - Tested 450°F - Hydrided Fasteners

Identity	Neolube	Torque Cycles	Fastener Test Concitions	Maximum Applied Tensile Stress (psi)*											
				Cycles #1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
#6	1	1	hydrided 4 days	4150	8300	12,500 ⁺	12,500	25,000 ⁺	25,000	37,500 ⁺	37,500	50,000 ⁺	50,000	62,500 ⁺	-----
#2	1	1	hydrided 11.3 days	4150	3300	12,500 ⁺	12,500	25,000 ⁺	25,000	37,500	25,000	37,500	50,000 ⁺	50,000	62,500 ⁺
#35	0	1	hydrided 7.3 days; 30 thermal cycles	4150 ⁺	4150	8,300	12,500	25,000 ⁺	25,000	37,500	50,000 ⁺	50,000	60,000 ⁺	79,500 ⁺	-----
#43	0	2	hydrided 7.3 days; 30 thermal cycles	12,500	12,500	25,000	25,000	37,500	37,500	50,000	50,000	60,000 ⁺	66,500 ⁺	-----	-----
A6**	0	1	hydrided 17.4 days	4150	8300	12,500	25,000 ⁺	25,000	37,500	50,000 ⁺	50,000	60,000 ⁺	-----	-----	-----
#4	1	1	hydrided 21.4 days	4150	8300	12,500	25,000 ⁺	25,000	37,500 ⁺	37,500	50,000 ⁺	60,000 ⁺	-----	-----	-----

*Calculated on a 0.02 in² bearing surface.

**Bearing surface intentionally smeared with Irconel-600 prior to fastener assembly.

+Fastener removed for inspection. All nuts were hand tight up to the 1000 lb (50,000 psi) load cycle.

TABLE VII
Compression Testing of 450°F - Hydrided Zircaloy-4 Tubing Segments

<u>Tubing Identity</u>	<u>Treatment</u>	<u>Autoclave Exposure Time (Days)</u>	<u>Compression Test Temperature (°F)</u>	<u>(0.2%) Compressive Yield Strength</u>	
				<u>lbs</u>	<u>psi*</u>
TU-1	Inconel-smeared bearing surface	4	70	1240	62,000
TU-2	Inconel-smeared bearing surface	4	500	610	30,500
T-2	Inconel-smeared bearing surface & O.C. & I.D. for 0.1"	7.3	70	1220	61,000
T-3	Inconel-smeared bearing surface & O.D. & I.D. for 0.1"	7.3	500	740	37,000

*Calculated on a 0.02 in² bearing surface.

TABLE VIII
X-Ray Diffraction Examination of 450°F - Hydrided Zircaloy-4 Samples

<u>Sample Identity</u>	<u>Sample Type</u>	<u>Treatment</u>	<u>Autoclave Exposure Time (days)</u>	<u>Intensity Ratio*</u>
L-3	Disassembled Small Diameter Nut	4 torque cycles; Inconel-smeared bearing surface	4	1.4
T-2	Tubing Segment	Inconel-smeared bearing surface & O.D. & I.D. for 0.1"	7.3	---
N-2	Unassembled Small Diameter Nut	Inconel-smeared on three surfaces	7.3	4.1
T-5	Tubing Segment	Inconel-smeared on three surfaces	17.4	10
S-5	Disassembled Small Diameter Nut	8 torque cycles; Inconel-smeared bearing surface	21.4	2.3
S-33	Disassembled Medium Diameter Nut	Inconel-smeared on three surfaces	34	2.4

*Integrated intensity ratios of the (220) diffraction peak of the delta phase to the (102) peak of the alpha phase.

TABLE IX
Hydriding of Small Diameter Fasteners at 520°F

Fastener Identity	Torque Cycles+	Autoclave Exposure Time (Days)	Hydride Rim Condition		Diffuse Rim Approximate Depth (Mils)**	Reference Figure Number
			Solid Rim, (Mils)			
			Depth	Crack-Length*		
111	2	34	1-2	None noted	15	---
114	2	63	7-10	15-17	20	23
117	2	88	<1	None noted	20	24
121	2	117	2-3	5	20	---
124	2	136	2-3	5	25	---
90	1	34	1-2	None noted	10	25
93	1	63	None noted	None noted	10	---
92	1	88	None noted	None noted	10-15	---
98	1	117	4-5	None noted	10-15	---
101	1	136	1-2	5	10-15	26

*Peripheral cracks observed in transverse section 1 mil below bearing surface. Cracks were very shallow (not observed in longitudinal sections).

**At 2000 ppm level based on a comparison of density of hydride platelets with metallographic standards.

+All fasteners were assembled without the use of Neolube lubricant.

TABLE X
Hydrogen Pickup of Small Diameter Nuts Autoclaved at 520°F

Spec. No.	No. of Assembly Torque Cycles	Autoclave Exposure (Days)	Best Fit ⁽¹⁾ Curve Constants		Area Under ⁽²⁾ Best Fit Curve, cm ²	Calculated H ₂ Pickup		
			A	B		ppm	mg	mg/dm ²
105	2	2	-	-	32.0	200	0.05	34
107	2	7	100 mil long			562	0.14	94
108	2	12	100 mil long			729	0.18	121
112	2	34	2239.4	- 0.05983	16.3	408	0.10	67
115	2	63	6714.9	- 0.06078	45.0	1125	0.28	187
118	2	88	4565.7	- 0.05306	33.8	845	0.21	141
122	2	117	4011.2	- 0.04851	32.7	818	0.20	134
123	2	136	3818.5	- 0.04477	32.3	809	0.20	134
83	1	2	100 mil long			141	0.035	23
84	1	7	-	-	32.3	202	0.05	34
85	1	12	100 mil long			634	0.16	107
94	1	63	2888.5	- 0.04907	24.5	613	0.15	101
95	1	88	3542.2	- 0.05351	26.6	665	0.16	107
99	1	117	2333.5	- 0.063164	27.4	685	0.17	114
100	1	136	1147.9	- 0.02639	14.5	363	0.09	60

NOTES: (1) Best fit curves for which constants are listed are given by $y_{ppm} = A \exp Bx$ (where x = depth from bearing surface in mils). For other specimens autoclaved less than 34 days, best fit curves were visually determined.

(2) From $x = 0$ to 100 mils as determined by planimeter integration.

TABLE XI
Autoclaving of Corrosion Control Coupons at 520°F

<u>Identity</u>	<u>Surface Condition</u>	<u>Autoclave Exposure Time (Days)</u>	<u>Post - Hydride Evaluation</u>		<u>Reference Figure No.</u>
			<u>Accelerated Hydriding</u>	<u>Solid Hydride</u>	
#4	Pickled	34	No	No	---
#16	Air-oxidized*	34	No	No	---
#17	Oxidized* and Inconel-smeared	34	Yes	No	30
#5	Pickled	63	No	No	---
#18	Air-oxidized*	63	No	No	---
#19	Oxidized* and Inconel-smeared	63	Yes	No	30
#6	Pickled	88	No	No	---
#20	Air-oxidized*	88	No	No	---
#21	Oxidized* and Inconel-smeared	88	Yes	No	30

* 2 hours at 750°F

TABLE XII
Small Diameter Fasteners for Thermal Cycling Tests

<u>Fastener Identity</u>	<u>Torque Cycles</u>	<u>520°F Autoclave Exposure Time (Days)</u>
91	1	34
113	2	34
137	3	34
144*	1	34
94	1	63
116	2	63
140	3	63
146*	1	63
96	1	88
119	2	88
141	3	88
148*	1	88
97	1	117
120	2	117
142	3	117
149*	1	117

*Bearing surface intentionally smeared with Inconel-600 prior to fastener assembly.

All fasteners were assembled without the use of Neolube lubricant.

TABLE XIII
Hydriding of Medium Diameter Fasteners

Fastener Identity	Fastener Assembly Variables			Washer Material	Cr-Plate Thickness (mils)	Hydriding Conditions			Reference Figure Number
	Neolubed	Torque Cycles	Final Rotation (Degrees)			Fastener Exposed Assembled	Autoclave Temperature (°F)	Exposure Time (Days)	
M-18	1	1	174	None	---	Yes	450	26.7	--
X-6	1	1	100	None	---	Yes	450	17	31
X-7	1	1	174	17 - 4 PH	bare	Yes	450	17	31
M-1	0	1	174	Inconel-600	0.04	Yes	450	7.3	32
M-2	0	1	174	Inconel-600	0.04	Yes	450	7.3	32
M-3	0	1	174	Inconel-600	0.04	Yes	450	17.4	32
M-4	0	1	174	Inconel-600	0.04	Yes	450	34	32
X-19	2	2	94	17 - 4 PH	bare	Yes	450	17	35
M-23	2	2	97	17 - 4 PH	0.2	Yes	450	17	35
X-8	2	2	96	17 - 4 PH	0.3	Yes	450	34	35
X-20*	2	2	94	17 - 4 PH	bare	Yes	450	17	35
M-24*	2	2	91	None	---	No	520	35	--
				17 - 4 PH	0.2	Yes	450	17	--
				None	---	No	520	35	--
M-21	1	1	100	17 - 4 PH	0.2	Yes	450	17	--
X-2	1	1	90	17 - 4 PH	0.3	Yes	450	17	--
X-10	1	1	100	17 - 4 PH	0.45	Yes	450	17	--
X-5	1	1	92	17 - 4 PH	0.3	Yes	450	34	--
M-22*	1	1	39	17 - 4 PH	0.2	Yes	450	17	--
X-4*	1	1	90	None		No	520	35	--
				17 - 4 PH	0.3	Yes	450	17	--
				None		No	520	35	--
M-11*	1	1	92	17 - 4 PH	0.4	Yes	450	17	--
				None		No	520	35	--
M-30	1	1	100	17- 4 PH	bare	No	520	35	--

*These assemblies were autoclaved for 17 days at 450°F. The nuts were disassembled by cutting and autoclaved for an additional 35 days at 520°F.

TABLE XIV
450°F - Hydrided Medium Diameter Nuts Torqued* Without a Chromium Barrier

Fastener Identity	Washer Material	Final Rotation (Degrees)	Exposure Time (Days)	Depth from Bearing Surface (mils)	Post - Test Hydride Condition		Estimated Maximum Local Hydrogen Content (ppm)
					Reference Figure Number	Sol'd Hydride Cracks	
M-18	None	174	26.7	0.9+	--	Yes	16,300+
				2.9+		Yes	16,300+
				3.9+		Yes	16,300+
				7.0+		No	7,000
				12.2+		No	3,000
				15.0+		No	2,300
				19.8+		No	1,000
X-6	None	100	17	1.0+	31	Yes	16,300+
				6.8++		Yes	16,300+
				11.0++		Yes	16,300+
				35.0++		No	1,000
X-7	Bare 17 - 4 PH	174	7	1.0+	31	Yes	16,300+
				2.8++		Yes	16,300+
				4.8++		Yes	16,300+
				16.0++		No	700

*Torqued once with Neolube and autoclaved assembled

+Transverse section

++Longitudinal section

TABLE XV
450°F - Hydrided Medium Diameter Nuts Torqued* on Cr-Plated+ Inconel Washers

Fastener Identity	Exposure Time (Days)	Depth from Bearing Surface (mils)	Post - Test Hydride Condition			Estimated Maximum Local Hydrogen Content (ppm)
			Reference Figure Number	Solid Hydride	Cracks	
M-1	7.3	1.0	32	Yes	No	16,300+
		2.0		No	No	12,000
		4.4		No	No	1,900
		5.5		No	No	500
		8.0		No	No	150
M-2	7.3	1.0	32	No	No	5,000
		3.0		No	No	200
M-3	17.4	1.0	32	No	No	6,200
		2.0		No	No	5,000
		3.0		No	No	550
M-4	34.0	1.1	32	Yes	Yes	16,300+
		3.1		Yes	No	16,300+
		5.3		No	No	5,000
		8.7		No	No	1,000
		10.8		No	No	550
		12.5		No	No	400

*Torqued once to 174° without Neolube and autoclaved assembled

+0.04 mil thick

TABLE XVI
Hydrided Medium Diameter Nuts Torqued Twice with Neolubed 17 - 4 PH Washers

Fastener Identity	Cr-Plating		Final Rotation (Degrees)	Final Torque (in-lb)	Hydriding Conditions			Depth from Bearing Surface (mils)	Reference Figure Number	Post - Test Hydride Content		
	Lot	Thickness (mil)			Fastener Exposed Assembled	Autoclave Temperature (°F)	Exposure Time (Days)			Solid Hydride	Cracks	Estimated Maximum Local Hydrogen Content (ppm)
X-19	---	bare	94	90	Yes	450	17	1	35	No	No	< 50
M-23	11A	0.2	97	93	Yes	450	17	1	35	No	No	< 50
X-8	11E	0.3	96	39	Yes	450	34	1	35	No	No	2,500
								4		No	No	900
								7		No	No	225
X-20	---	bare	94	103	Yes	450	17	---	35	No	No	---
					No	520	35	1		No	No	6,000
								4		No	No	5,000
								7		No	No	3,500
								10		No	No	1,900
								16		No	No	200
M-24	11A	0.2	91	90	Yes	450		---	--	---	---	---
					No	520		1		No	No	< 50

TABLE XVII
Hydrided Medium Diameter Nuts Torqued Once with Neolubed 17 - 4 PH Washers

Fastener Identity	Cr-Plating		Final Rotation (Degrees)	Final Torque (in-lb)	Hydriding Conditions			Post-Test Hydride Content (ppm)
	Lot	Thickness (mil)			Fastener Exposed Assembled	Autoclave Temperature (°F)	Exposure Time (Days)	
M-21	11A	0.2	100	100	Yes	450	17	<50
X-2	11E	0.3	90	103	Yes	450	17	<50
X-10	11D	0.45	100	100	Yes	450	17	<50
X-5	11E	0.3	92	108	Yes	450	34	<50
M-22	11A	0.2	89	105	Yes	450	17	--
					No	520	35	<50
X-4	11E	0.3	90	108	Yes	450	17	--
					No	520	35	<50
X-11	11D	0.4	92	117	Yes	450	17	--
					No	520	35	<50
M-30	---	bare	100	100	No	520	35	<50

TABLE XVIII
Hydriding Behavior of Nuts Assembled with Bare 17 - 4 PH Washers

<u>Fastener Identity</u>	<u>Assembly Conditions*</u>		<u>Hydriding Conditions</u>			<u>Post - Test Hydride Content</u>		
	<u>Torque Cycles</u>	<u>Final Rotation (Degrees)</u>	<u>Fastener Exposed Assembled</u>	<u>Autoclave Temperature (°F)</u>	<u>Exposure Time (Days)</u>	<u>Maximum Hydrogen (ppm)</u>	<u>Depth Hydrogen >500 ppm (mils)</u>	<u>Reference Table</u>
X-7	1	174	Yes	450	17	16,300+	16	XIV
M-30	1	100	No	520	35	< 50	--	XVII
X-19	2	94	Yes	450	17	< 50	--	XVI
X-20	2	94	Yes	450	17	---	--	XVI
			No	520	35	6,000	16	

*Neolube lubrication used for all specimens during assembly

Figure 1

Medium Diameter Fasteners Assembled and Autoclaved at 450°F for 17 Days

Figure 2

Distribution of Nickel on Contacting Surface of Zircaloy-4 Nut 22.
Electron Microprobe Nickel Image Produced at 167X and Reduced to Approximately 28:

Hydrided Nut #6
(Neolubed; 1 Torque; 4 Days
Exposure at 450°F

A. Bearing Surface 10X

B. 0.5 Mil Depth Overall
View 10X

C. Hydride Condition at
12 O'Clock Position
100X

Figure 3

FIGURE 4
AXIAL DISTRIBUTION OF HYDROGEN
IN SINGLE TORQUED SMALL DIAMETER NUTS HYDRIDED AT 450°F

FIGURE 5
AXIAL DISTRIBUTION OF HYDROGEN IN DOUBLE TORQUED SMALL DIAMETER NUTS HYDRIDED
AT 450 °F

Figure 6

Nut #10: 4 Days Exposure

A. Bearing Surface 10X

B. 0.4 Mil Depth 10X

Nut #9: 11.3 Days Exposure

C. Bearing Surface 10X

D. 0.5 Mil Depth 10X

Small Diameter Nuts (Neolubed Once; 3 Torques) Hydrided at 450°F

FIGURE 7
AXIAL DISTRIBUTION OF HYDROGEN IN NEOLUBED
TORQUED SMALL DIAMETER NUTS HYDRIDED AT 450° F

FIGURE 8
EFFECTIVENESS OF NEOLUBE LUBRICANT IN MINIMIZING ACCELERATED
HYDRIDING AT 450°F OF SMALL DIAMETER NUTS (0.5 - 1 MIL BELOW BEARING SURFACE)

Figure 9

Nut #L2 (Neolubed; 4 Torques) Hydrided Disassembled for Four Days at 450°F
(1 Mil Depth)

Figure 10

Nut 14: Neolubed Once; 6 Torques

A. Bearing Surface 8X

B. 5 Mils Depth 10X

Nut N1: Inconel Smearcd; No Neolube; No Torquing

C. Bearing Surface 8X

D. 5.2 Mils Depth 10X

Disassembled Small Diameter Nuts Hydrided at 450°F for 7.3 Days

Figure 11

Coupon #2: Autoclaved for 10.1 Days

A.

100X

B.

500X

Coupon #3: Autoclaved for 26.7 Days

C.

100X

D.

250X

Pickled Zircaloy-4 Control Coupons Hydrided at 450°F

Figure 12

A.

#11 Hydrided for 7.3 Days 30X

x100

x100

x100

x100

x100

B. #13 Hydrided for 10.1 Days

Inconel-Smeared Corrosion Coupons Hydrided at 450°F

FIGURE 13

Figure 14

A. 1 Mil Depth 10X

B. 29 Mils Depth 10X

C. Longitudinal Section 100X
After 29 Mils Grinding

Inconel-Smeared Nut A 10 Hydrided for 34 Days at 450°F

A. #25

B. #26

Figure 15

Appearance of Zircaloy Nut/Inconel Plate
Contact Region Specimens #25 and #26
(Hydrided 17.4 days) after 10 Thermal Cycles

C. Max. Deformed Region, #25 X20

D. Gap Region, #25 X20

E. Max. Deformed Region, #26

F. Gap Region, #26 X20

A. #25

B. #26

Figure 16

Appearance of Zircaloy Nut/Inconel Plate
Contact Region of Specimens #25 and #26
(Hydried 17.4 days) after 30 Thermal
Cycles

C. Max. Deformed Region, #25 X20

D. Gap Region, #25 X20

E. Max. Deformed Region, #26 X20

F. Gap Region, #26 X20

A. As-Hydrided

After 30 Thermal Cycles

B. As-Hydrided (34 Days at 450°)

C. After 10 Thermal Cycles

D. After 20 Thermal Cycles

Appearance of Deformed and Gap Regions of Fastener #70

20X

Figure 17

Figure 18

A. As-Hydrided (34 Days at 450°F)

B. After 10 Thermal Cycles

C. After 20 Thermal Cycles

D. After 30 Thermal Cycles

FIGURE 19
SCHEMATIC OF LOADING ARRANGEMENT OF
HYDRIDED FASTENERS

Figure 20

A. Bearing Surface 10X

B. 1 Mil Depth 10X

C. 2 Mils Depth 10X

D. Longitudinal Section 100X
After 2 Mils Grinding

Inconel-Smeared Nut A6 Hydrided for 17.4 Days at 450°F and Tensile Tested

Figure 21

A. Bearing Surface 10X

B. Bearing Surface 25X

C. 2 Mil Depth 10X

D. Longitudinal Section
After 2 Mils Grinding 100X

Nut #4 Hydrided for 21.4 Days at 450°F and Tensile Tested

Figure 22

X10

X25

A. As Hydrided Tube End

X10

B. After Loading in Compression to 70lbs at 500°F

Inconel-Smeared Tubing Hydrided for 4 Days at 450°

Figure 23

A. 1 Mil below Bearing Surface 10X

B. Most Severe Hydrided Region 100X
1 Mil below Bearing Surface C. Longitudinal Section at 1 to 7.5
mils below Bearing Surface 100X

Hydrided appearance of nut #114 assembled using two torque cycles and autoclaved 63 days at 520°F

Figure 24

A. 1 Mil below Bearing Surface 10X

B. Most Severe Hydrided Region 100X
1 Mil below Bearing Surface C. Longitudinal Section at 1 to 7.5
mils below Bearing Surface 100X

Hydrided appearance of nut #117 assembled using two torque cycles,
autoclaved 88 days at 520°F

Figure 25

10X

A. 1 mil below bearing surface

100X

B. Most severe hydrided region
1 mil below bearing surface C. Longitudinal section at
3.4 to 10 mils below bearing
surface 100X

Hydrided appearance of nut #90 assembled using one torque cycle and
autoclaved 34 days at 520°F

Figure 26

10X

A. 0.5 - 1 mil below bearing surface

100X

B. Most severe hydrided region
0.5 - 1 mil below bearing surface

100X

C. Longitudinal section at 1 to
7.5 mils below bearing surface

Hydrided appearance of nut #101 assembled using one torque cycle and
autoclaved 136 days

HYDROGEN DISTRIBUTION IN ZIRCALLOY-4 NUTS TORQUED TWICE AGAINST AN INCONEL-600 PLATE AND AUTOCLAVED FOR VARIOUS TIMES

FIGURE 27

HYDROGEN DISTRIBUTION IN ZIRCALOY-4 NUTS TORQUED ONCE AGAINST AN INCONEL-600 PLATE AND AUTOCLAVED FOR VARIOUS TIMES

FIGURE 28

HYDROGEN PICKUP VS AUTOCLAVE EXPOSURE

FIGURE 29

Figure 30

A. #17: 34 days exposure 100X

B. #19: 63 days exposure 100X

C. #21: 88 days exposure 100X

D. #21: 88 days exposure 100X

Inconel-Smeared Zircaloy-4 Coupons Hydrided at 520^oF

A. X-6 7X

B. X-7 7X

C. X-6 100X

D. X-7 100X

Neolubed Medium Diameter Nuts Hydrided for 17 Days at 450°F Without A Chromium Barrier

A. M-1; 7.3 Days 8X

B. M-2; 7.3 Days 8X

C. M-3; 17.4 Days 8X

D. M-4; 34 Days 8X

Medium Diameter Nuts Torqued with Chromium-Plated Inconel Washers and Hydrided at 450°F

FIGURE 33
FASTENER ASSEMBLIES HYDRIDED WITH
CR-PLATED INCONEL WASHERS AT 450°F

M-1

B.

M-2

M-3

D.

M-4

Chromium-Coated Inconel Washers (1000X)

Figure 35

A. X-19: 17 Days

300X

B. M-23: 17 Days

300X

C. X-8: 34 Days

7X

D. X-20: 17 Days

7X

Medium Diameter Nuts Double-Torqued with 17 - 4 Washers and Hydrided at 450°F (1 mil depth)

APPENDIX A

ZIRCALOY FASTENER ASSEMBLY DETAILS

The fastener assembly consists of a long Zircaloy-4 stem which fits through a hole in an Inconel-600 support plate. A Zircaloy sleeve fits over the stem and into a countersunk recess in the Inconel plate. As illustrated in Figure A-1, internal threads in the sleeve engage external threads on the stem. While the stem is prevented from rotation, a torque is applied to the sleeve and the assembly is thereby fastened securely to the Inconel plate. This is done by first applying a measured torque to seat the parts and then rotating the sleeve through a measured angle. This angle is chosen so as to apply a preload in the sleeve and stem large enough to accommodate thermal and radiation induced relaxation in the Zircaloy.

The minimum assembly preload stresses are at or slightly below yield. When the reactor is heated up to operating temperature, the Inconel-600 expands more than the Zircaloy-4 (see Table I). This relative expansion additionally compresses the sleeve axially, and, assuming that the friction between the sleeve and Inconel plate prevents relative radial motion, which sometimes occurred in the test fasteners, pulls the open end of the sleeve outward. The axial compression of the sleeve imparts additional tensile stretch on the stem.

The fastener assembly variables and representative loadings in the various types of Zircaloy nuts are compared in Table A-1.

TABLE A-1
Test Fastener Assembly Data

<u>Property</u>	<u>Fastener Type</u>			
	<u>Small*</u>		<u>Medium**</u>	<u>Large+</u>
	<u>Short Length</u>	<u>Standard Length</u>		
Initial Torque (± 1 in-lb)	22	22	15	15
Angle of Rotation (+4/-0 Degrees)	60	55	100,174	114
Estimated Total Assembly Torque (in-lb)	80	60	100-190	120-130
Nut Loadings				
Force (lb)	846	770	1550	1685
Strain (%)	0.55	0.38	0.35	0.58
Bearing Stress (psi)	87,000	80,000	42,000	34,000

*0.3 in. Diameter

**0.6 in. Diameter

+0.8 in. Diameter

FIGURE A-1

FASTENER ASSEMBLY

APPENDIX B

SUPPLEMENTARY DATA AND PHOTOMICROGRAPHS ON INCONEL TRANSFER

I. Chemical Analyses

Nickel transfer from the Inconel plate to the Zircaloy nut contacting surface during single and multiple fastener assembly operations was evaluated for one large diameter and eight small diameter nuts. The test samples, listed in Table B-I, had received from one half to eight torque cycles. A torque cycle consisted of a pretorque load, a torque rotation, and the complete detorquing. A sample with one half a torque cycle was cut off at the end stem to prevent further Inconel transfer had the nut been removed by detorquing.

The electron microprobe, X-ray fluorescence spectrometer and spark source mass spectrometer results also are given in Table B-I. Except for the untorqued, but prefilled, control sample, nickel was detected on the contact surface of all the disassembled Zircaloy nuts. As illustrated in Figure 2, nickel was found by electron microprobe examination to be distributed non-uniformly over the entire contacting surface of small diameter nut 22. Analysis of the bearing surface of large diameter nut 1C2 by X-ray fluorescence spectrometry showed the presence of the other constituents in Inconel besides nickel, thus demonstrating the transfer to the nut of Inconel from the plate. Inconel transfer was confirmed by a comparison of the spectrum of an Inconel standard with those from the surface of small diameter nuts L1 and L5. The spectra were obtained with the energy dispersive spectrometer of the electron microprobe and are shown in Figure B-1.

Macroscopic examination of the contacting surface of the disassembled nuts helped explain the variable amounts of nickel transferred. During the torquing operation the rod nuts slip on the Inconel plate; the amount of slippage observed on the test samples varied from only a few mils up to a maximum of about 30 mils. This

slippage caused plastic flow of the contacting surface of the rod nuts and removal of the zirconium oxide film, thus permitting Zircaloy to come in contact with Inconel. The detorquing operation causes even more damage to the contact surface. During detorquing the plastically deformed Zircaloy can now either be sheared off or undergo plastic flow in the opposite direction. This removes even more of the Zirconium oxide film and permits more Zircaloy to come into intimate contact with Inconel.

II. Transfer and Bonding Measurements

A. Small Diameter Nuts

Quantitative information was obtained on transfer and bonding of Inconel to the bearing surface of Zircaloy small diameter nuts as affected by torquing during fastener assembly.

Three disassembled torqued Zircaloy small diameter nuts, described in Table II, were pressure mounted longitudinally and ground through their entire 0.3-inch diameter contact surface in ten 30-mil increments. The cross section of the bearing surface thus exposed was examined at each stage in the as-polished and etched condition and photomicrographs were taken to illustrate significant differences in degree and intimacy of contact at the Zircaloy/Inconel interface.

The initial grinding step was for 10 mils below the nut external periphery and very little (approximately 10 percent) corrosion ZrO_2 film was observed on the nut contacting surface of all three samples at this level examined. However, intact ZrO_2 films were present on the nut surfaces which did not contact the Inconel-600 plate bearing surfaces, i.e., perpendicular to the bearing surface. In the as-polished condition, surface damage and some transferred Inconel -- more apparent in the multi-cycled torque sample (Figure B-2A and B-2C) -- were observed on the smeared contacting surfaces of all three samples.

All of the second phase can be seen more clearly after a strong acid (HNO_3/HF /Oxalic Acid) stain etch, as shown in Figures B-2B and B-2D. In addition, most of this second phase is attacked by a hydrochloric acid/copper sulfate (Marble's reagent) etch for Inconel as shown in Figure B-3. These etching results confirm electron microprobe and other chemical analyses showing the presence of nickel and Inconel on the contact surface of torqued small diameter nuts and indicate that the observed deposit on the deformed Zircaloy surface is smeared Inconel.

As the grinding continued, considerable ZrO_2 film was found to be retained on the contacting surface in contrast to the observed absence of a ZrO_2 film for the initial grinding step. Zirconium oxide film rupture and transferred Inconel were generally found at or near the outside diameter regions of the contacting surfaces. However, the transferred Inconel often appeared to be unbonded, i.e., not in intimate contact with the Zircaloy bearing surfaces, as illustrated in Figure B-4.

Attempts were made to estimate from the photomicrographs the linear amount of Zircaloy contact surface with a protective ZrO_2 film, the amount of bare surface and the fraction of surface in contact with the transferred Inconel.

Some transferred Inconel was observed at each grinding level on the contacting surfaces of all three nuts. The transferred Inconel was distributed non-uniformly over the contact surface of each nut and the Inconel concentration was quite variable. This is in agreement with the electron microprobe X-ray image analyses where the Inconel was found inhomogeneously spread over a small diameter nut bearing surface, apparently taking on a circular path consistent with the rotary motion during torquing.

In this study, as seen from Table II, the observed transferred Inconel was a small fraction (≤ 20 percent) of the contact surface and about half of this Inconel was unbonded, i.e., not in intimate contact with the Zircaloy bearing surface (Figure B-4). A typical bonded Inconel region was approximately 0.5 mil long and about 0.1 mil thick. The longest bonded Inconel region observed was around 4.5 mils and the thickest deposit was 0.5 mil.

Finally, statistical analyses were made on the percent of both total Inconel transferred and bonded Inconel for the three sectioned torqued small diameter nuts. The measurements were processed in a standard manner using a computer program which assumed constant variance. The resulting averages were found to be statistically different at the 5 percent significance level, i.e., the differences in the averages among the three samples were real. However, the metallographic data indicated non-constancy of variance within each nut, as well as some non-normality of the distribution. Because of this, the measurements were re-analyzed by the computer program with a square root transformation. When the data were transformed to a square-root scale, there was no evidence of non-constancy of variance or non-normality. The resulting three averages, which again were statistically significantly different, were squared to return them to their original units and are presented in Table II together with their 95 percent confidence intervals. Although the results obtained via square-root transformation are not notably different from those obtained by the original procedure, they are preferred in that the underlying assumptions of the analysis of variance appear to be better satisfied.

The data in Table II indicate that the percent of bearing surface identified with both total transferred Inconel and bonded Inconel was significantly affected by torquing operations, increasing with the number of torque cycles and amount of lateral displacement of the nut

during torquing. For example, the average percentage of total transferred Inconel increased from 3.82 percent to 8.53 percent to 15.46 percent of the nut bearing surface for one torque cycle with minimum displacement, one torque cycle with 30 mils lateral slippage and three torque cycles with 30 mils displacement, respectively. The corresponding values for bonded Inconel were 1.94, 4.10 and 8.43 percent, respectively, i.e., about half the total transferred Inconel values.

B. End Stems

As discussed above, Inconel is transferred from the Inconel-600 plate to the contacting surface of Zircaloy-4 nuts during assembly of the fasteners due to the relative circumferential and radial movement of these components. In case of the end stem/Inconel-600 plate contact regions (see Figure A-1), no radial motion normally occurs during assembly. Because fuel rods must pass through the grids before the end stems contact the Inconel-600 plate during assembly, cocking of the rods (hence the end stems) and rubbing of components does not occur in core rod assembly operations. However, such relative motion can occur inadvertently during assembly of test specimens. A test was performed on a standard length small diameter nut, inadvertently misaligned during assembly, to find out whether this type of rubbing action was sufficiently severe to remove the protective corrosion oxide film and allow some transfer and bonding of Inconel to occur.

Zircaloy-4 nut #22, which was assembled with Neolube and torqued one time on an Inconel plate, was cut off at the end stem as previously described (Table B-I) to avoid any further Inconel transfer during assembly. The surface of the end stem that was in contact with the Inconel plate is illustrated in Figure B-5. The circumference of the

end stem was inadvertently deformed in two locations due to abnormal misalignment during assembly of this specific test end connector. The minute parallel scratches clearly visible on the contacting surface of the end stem, as shown in Figure B-5, are replicas of the machining marks on the surface of the Inconel plate which were impressed on the contacting surface of the Zircaloy-4 end stem when the nut was torqued on the opposite side of the plate. This indicates that the end stem did not rotate against the Inconel plate. If the end stem had rotated against the Inconel plate, these scratches (or impressions) would have been smeared rather than having distinctly sharp edges.

An electron microprobe (X-ray fluorescence image) analysis of the contacting surface of the end stem revealed a considerable concentration of nickel (Inconel) in the areas marked A and B in Figure B-5. These are the two areas on the circumference of the end stem where the metal was deformed by contact with the Inconel-600 baseplate. Radial Ni X-ray images 90° apart were taken at specific circumferential locations (Areas A, B, C, and D) and also are shown in Figure B-5 for areas A and B. They verify that Ni contamination is present as a function of the extent of gouging, i.e., where the gouging is severe the contamination is heavy, and there is little contamination where the gouging is light or absent. In this end stem specimen, the gouging is almost exclusively circumferential, as is the Ni contamination.

Metallographic examination of the as-polished end-stem surface showed some surface damage and the presence of a surface deposit, restricted to relatively small areas (approximately 10 percent of the deformed surface) on one of the chamfered edges. This deposit, as shown in Figure B-6A, appeared to be bonded, i.e., in intimate contact with the Zircaloy-4 bearing surface, in some but not all places and covered about 7 percent of the contact surface. The deposit contrast was enhanced by a Zircaloy stain etch (Figure B-6B) and was severely attacked by both electrolytic phosphoric acid or immersion in CuSO_4 and hydrochloric acid (Marble's Reagent) (Figure B-6C). These etching results confirm the electron microprobe analyses in demonstrating that the deposit is transferred Inconel.

TABLE B-I
Analysis of Zircaloy Nut Contact Surface for Nickel Transfer During Assembly and Disassembly

<u>Nut Identity</u>	<u>Assembly Method</u>	<u>Analysis Method</u>	<u>Inspection Results</u>
Prefilmed small diameter control nut	Not assembled	Electron microprobe (4 traces)	No nickel
Large diameter nut 1C2	1 torque cycle	Electron microprobe (4 traces) X-ray fluorescence (360° trace) Mass spectrograph (several spot traces)	Nickel detected Inconel detected on entire surface <u>> 10% nickel</u>
Standard length small diameter nut 6K14	1 torque cycle	Electron microprobe (4 traces) Mass spectrograph (180° trace)	Nickel detected 19% nickel
Standard length small diameter nut L-1	3 torque cycles	Electron microprobe (4 traces) Mass spectrograph (180° trace)	Nickel detected 16% nickel
Standard length small diameter nut L-5	8 torque cycles	Electron microprobe (4 traces) Mass spectrograph (180° trace)	Nickel detected 5% nickel
Small diameter nut A	1/2 torque cycle	Electron microprobe (4 traces)	Nickel detected
Small diameter nut B	1/2 torque cycle	Electron microprobe (4 traces) Mass spectrograph (180° traces)	Nickel detected 17% nickel
Small diameter nut C	1/2 torque cycle	Electron microprobe (4 traces)	Nickel detected
Standard length small diameter nut 22	1/2 torque cycle	Electron microprobe (360° trace) Mass spectrograph (4 90° traces)	Nickel detected over entire surface 6%, 3%, 5%, 5% nickel

Figure B-1

Zircaloy-4

Nut L-1

Zircaloy-4

Nut L-5

Inconel Standard

Figure B-2

A. As-Polished 1000X

B. Stain-Etched 1000X

C. As-Polished 1000X

D. Stain-Etched 1000X

Triple-Torqued Nut #5

Figure B-3

A

As-Polished

750X

B

Inconel-etched: Marble's Reagent

500X

Multi-Cycled Torqued Zircaloy Nut #5

Figure B-4

A.

As-Polished

1000X

B. As-Polished

1500X

C. Stain-etched

1500X

Multi-Cycled Torqued Zircaloy Nut #5

Figure B-4 (Cont'd)

A.

As-Polished

1000X

B. As-Polished

500X

F. Stain-etched

750X

10X

Zircaloy-4 End Stem #22 showing parallel scratches on contacting surface and two deformed areas (A and B) where nickel was detected

Area A

167X

Area B

167X

Electron Microprobe A-ray Image Scan for Nickel, Indicating Inconel Transfer in Locations A & B Above

Figure B-6

A.

As-Polished

1500X

B. Stain-etched 1500X

C. Marble's Reagent Etch 1500X

Section of Zircaloy-4 End Stem #22

APPENDIX C

SUPPLEMENTARY SUMMARY TABLES AND PHOTOMICROGRAPHS OF AUTOCLAVED HYDRIDED TEST SPECIMENS

I. 450°F Autoclave Tests

A. Zircaloy Fasteners

The post-test hydride examination results for the single and multi-torqued small diameter nuts are listed in Tables C-I and C-II.

The axial depths of the local solid hydride rims were not constant for most of the multi-torqued fasteners. This indicates that the total hydrogen and/or the hydrogen ingress rates varied in these regions. This could result from variations in the area of the bonded Inconel, possible interconnection with adjacent unbonded Inconel and thinning of otherwise thicker and less hydrogen permeable zirconium oxide film during the fastener assembly operations.

B. Corrosion Control Coupons

The appearance of the Inconel-smear Zircaloy-4 coupons before (#29) and after clamping and hydriding (#15) is compared in Figures C-1 and C-2.

II. 520°F Autoclave Tests

A. Zircaloy Fasteners

The metallographically estimated hydrogen distribution for single-torqued small diameter nut #90 is plotted in Figure C-3. The hydride rim, mostly diffuse, is approximately 20 mils deep. The average hydrogen content within this depth is about 4000 ppm.

TABLE C-I
Single Torqued Small Diameter Nuts Hydrided Assembled at 450°F

Fastener Identity	Neolubed	Hydriding Time (Days)	Depth from Bearing Surface (mils)	Post - Test Hydride Conditions		
				Solid Hydride	Cracks Present	Estimated Maximum Local Hydrogen Content (ppm)
#6	Yes	4	0.5	Yes	No	16,300+
			1.9	No	No	3,000
			3.9	No	No	500
			5.4	No	No	300
			7.8	No	No	100
#2	Yes	11.3	0.4	Yes	Yes	16,300+
			1.4	Yes	No	16,300+
			2.4	No	No	5,000
			3.7	No	No	3,000
			5.6	No	No	2,000
			7.6	No	No	350
#157	Yes	10.1	9.7	No	No	250
			0.6	Yes	Yes	16,300+
			1.4	Yes	Yes	16,300+
			2.6	Yes	Yes	16,300+
			4.3	Yes	Yes	16,300+
			5.3	Yes	Yes	16,300+
			6.4	Yes	Yes	16,300+
			9.1	Yes	No	16,300+
			12.3	No	No	6,000
			16.3	No	No	5,000
			18.8	No	No	3,000
			23.3	No	No	150

TABLE C-I (continued)

Fastener Identity	Neolubed	Hydriding Time (Days)	Post - Test Hydride Conditions			
			Depth from Bearing Surface (mils)	Solid Hydride	Cracks Present	Estimated Maximum Local Hydrogen Content (ppm)
#35	No	7.3	1.0	Yes	Yes	16,300+
			1.7	Yes	Yes	16,300+
			3.7	Yes	No	16,300+
			5.0	No	No	6,000
			6.8	No	No	4,000
			10.8	No	No	250
			12.9	No	No	150
#81	No	10.1	1.1	Yes	Yes	16,300+
			1.7	Yes	Yes	16,300+
			4.7	Yes	Yes	16,300+
			6.7	Yes	Yes	16,300+
			7.9	Yes	No	16,300+
			10.4	No	No	10,000
			12.2	No	No	5,000
			15.0	No	No	3,000
			16.9	No	No	1,000
			19.3	No	No	150

TABLE C-II
Multi-Torqued Small Diameter Nuts Hydrided Assembled at 450°F

Fastener Identity	Neolubed	Torque Cycles	Hydriding Time (Days)	Post - Test Hydride Conditions			
				Depth from Bearing Surface (mils)	Solid Hydride	Cracks Present	Estimated Maximum Local Hydrogen Content (ppm)
#173	2	2	10.1	1.0	Yes	Yes	16,300+
				3.7	Yes	Yes	16,300+
				6.7	Yes	Yes	16,300+
				8.0	Yes	Yes	16,300+
				10.0	No	No	6,000
				12.5	No	No	3,000
				14.8	No	No	2,000
				17.3	No	No	500
#163	1	2	10.1	0.9	Yes	Yes	16,300+
				1.6	Yes	Yes	16,300+
				4.1	Yes	Yes	16,300+
				7.1	Yes	No	16,300+
				8.8	Yes	No	16,300+
				12.2	No	No	14,000
				15.7	No	No	5,000
#43	0	2	7.3	1.0	Yes	Yes	16,300+
				1.7	Yes	Yes	16,300+
				5.2	Yes	Yes	16,300+
				8.2	Yes	No	16,300+
				9.2	No	No	16,300+
				11.8	No	No	6,000
				14.8	No	No	4,000
				17.9	No	No	3,000
				20.4	No	No	500
				22.9	No	No	200

TABLE C-II (continued)

Fastener Identity	Neolubed	Torque Cycles	Hydr- ding Time (Days)	Post - Test Hydride Conditions			
				Depth from Bearing Surface (mils)	Solid Hydride	Cracks Present	Estimated Maximum Local Hydrogen Content (ppm)
#64	0	2	17.4	1.1	Yes	Yes	16,300+
				2.4	Yes	Yes	16,300+
				6.4	Yes	Yes	16,300+
				11.7	Yes	Yes	16,300+
				17.2	Yes	No	16,300+
				19.2	Yes	No	16,300+
				21.7	No	No	6,000
				24.4	No	No	4,000
				27.4	No	No	3,000
#10	1	3	4	31.6	No	No	300
				0.5	Yes	Yes	16,300+
				2.2	Yes	Yes	16,300+
				4.6	Yes	Yes	16,300+
				6.6	Yes	Yes	16,300+
				9.6	Yes	Yes	16,300+
#9	1	3	11.3	11.6	No	No	1,000
				0.5	Yes	Yes	16,300+
				2.6	Yes	Yes	16,300+
				4.6	Yes	Yes	16,300+
				7.3	Yes	No	16,300+
				9.9	Yes	No	16,300+
				12.3	No	No	4,000
#9	1	3	11.3	14.3	No	No	1,000

Figure C-1

A. As-Polished 250X

B. Stain-Etched 250X

C. As-Polished 250X

D. Stain-Etched 250X

Inconel-Smeared Zircaloy-4 Coupon #29

Figure C-2

A.

250X

B.

250X

C.

250X

D.

250X

Inconel-Smeared Zircaloy-4 Coupon #15 Hydrided for 26.7 Days at 450°F

FIGURE C-3
HYDROGEN DISTRIBUTION IN NUT NO. 90°
HYDRIDED FOR 34 DAYS AT 520°F

APPENDIX D

HYDROGEN CONTENTS OF 520°F - HYDRIDED ZIRCALOY-4 NUTS

Fifteen Zircaloy-4 nuts, autoclaved from 2 to 136 days, were disassembled and chips were machined for chemical hydrogen analyses.

The hydrogen values were plotted vs distance and the visually determined best fit curves were drawn through the data on one sheet to first rapidly obtain an indication of the effect of exposure time on total hydrogen pickup. Subsequently a computer program was used to identify the optimal least squares model from among six different curve types. The curve type which best fitted the data for all samples was given by the following equation:

$$y = A \exp Bx \quad \text{where } y = [\text{H}_2] \text{ in ppm}$$

x = distance below bearing surface, in mils
 $A \& B$ = constants determined for individual specimens
and exposure times

Representative curves are illustrated in Figures D-1 and D-2. Using the best fit curves, the area under each curve, from $x = 0$ to $x = 100$ mils, was measured with a planimeter. This permitted calculating the total hydrogen pickup in mg/dm^2 of bearing area for each nut. The 100 mil depth below the bearing surface was selected since all curves appeared to converge to about 25 ppm (the assumed base hydrogen value for the as-corrosion-filmed Zircaloy). The total ppm hydrogen pickup obtained via planimeter measurements agreed very closely with values calculated via integration of the least squares fitted equations.

AVERAGE HYDROGEN IN CHIPS MACHINED FOR 5 MIL INCREMENTS STARTING
AT BEARING SURFACE OF NUT NO. 123

FIGURE D-1

AVERAGE HYDROGEN IN CHIPS MACHINED FOR 5 MIL INCREMENTS STARTING
AT BEARING SURFACE OF NUT NO.100

FIGURE D-2

APPENDIX E

ELECTRON MICROPROBE ANALYSES OF MEDIUM DIAMETER NUTS TORQUED WITH METAL ALLOY WASHERS

A. Nuts Torqued with Chromium-Plated Inconel Washers

Five medium diameter nuts with thin (~ 0.04 mil) chromium-plated metal alloy washers (four Inconel-600 and one 304 stainless steel) were pretorqued 15 inch-pounds and then given a final high torque rotation of 174 degrees. The fasteners were disassembled for evaluation of material transfer without autoclave exposure. Pertinent assembly data and electron microscope findings are listed in Table E-I. Visual examination of the nut and washer contact surfaces after torquing showed some scoring.

The contact surfaces of three nuts torqued without Neolube lubricant were analyzed for Inconel transfer over a wide area by electron microprobing (EMP). Results are given in Table E-I. Elemental X-ray images, obtained by electron beam scanning of four gouged areas on each nut, disclosed the distribution of the metallic contaminations on the Zircaloy surfaces contacting the Cr-plated washers. Some typical electron microprobe features are illustrated in Figure E-1 for nut I-1.

Chromium from the plating was detected on the surfaces of all three nuts. EMP examination showed the presence of nickel in the gouged regions of the two nuts torqued with the Inconel washers. Limited qualitative analysis by energy dispersive X-ray spectrometry confirmed that the composition of the Ni-bearing particles on the Zircaloy contacting surfaces of both nuts is the same as that of an Inconel-600 standard (Figure E-1D). More Inconel particles were detected on the nut torqued once -- in agreement with the more heavily scored appearance of its contact surface. However, the amount and distribution (area coverage) of Inconel on the contacting surfaces of both nuts was not as widespread as was previously observed on nuts torqued without Cr-plated washers (Section III A; Appendix B).

EMP examination showed that little, if any, nickel was transferred from the Cr-plated stainless steel washer to the contact surface of Zircaloy nut SS-1. Chromium from the plating and some Ni-free iron contaminant particles were detected but only one stainless steel particle (0.4 mil in diameter) was observed on the scored Zircaloy bearing surface.

Radial scans of the contact surfaces of the two nuts torqued with Neolube lubricant were performed at 0, 90, 180 and 270 degrees. Inconel transfer was observed for both samples and appeared to be greatest at the regions of heavy gouging of the double-torqued nut I-25. Much of the Inconel pickup on the single-torqued nut I-18 was particulate. The bearing surface was examined at high magnification (500X) and little or no evidence of loss of integrity, i.e., local removal, of the ZrO_2 corrosion film was observed. Contaminants identified as a 300 series stainless steel and a low alloy or carbon steel were found also on nut I-18. As discussed below, some 300-type stainless steel particles were detected on a nut torqued with a Cr-plated 17 - 4 PH washer. This suggests that contamination, possibly by the stainless steel tooling used during fastener assembly, may have occurred.

B. Nuts Torqued with 17 - 4 PH Washers

Four medium diameter nuts were torqued once, one against a bare 17 - 4 PH washer and three others against Cr-plated 17 - 4 PH washers. The washers were placed between the nut and an Inconel support plate. Both sides of each washer were Neolubed. The nuts were pretorqued 15 inch-pounds and then given final torque rotations of 90 to 176 degrees. Pertinent assembly data are listed in Table E-II. Following nut tightening, the sleeves of the nuts were cut and the threaded sections were removed without any counter rotation. The contact surface of the nuts were examined by EMP techniques and the results are given in Table E-II.

The alloy 17 - 4 PH was transferred from the bare washer to its nut contacting surface (M-30). Four areas 90° apart were examined and X-ray image montages were prepared covering the surface at each area from the O.D. to the I.D. Since iron is the major constituent of 17 - 4 PH, Fe X-rays were used for imaging. To verify that the Fe contaminant found was 17 - 4 PH, a high Fe inclusion in each area was analyzed with the microprobe's energy dispersive system and the resulting spectra matched that of a 17 - 4 PH reference standard. The EMP results showed general heavy contamination at both the nut O.D. and I.D. In addition, the regions of heavy gouging were also regions of heavy 17 - 4 PH transfer.

Nut M-25, torqued to 90° with a Cr-plated 17 - 4 PH washer, was examined at 28 spots in the gouged regions, randomly selected around the entire surface. The EMP analyses showed the presence of free Cr from the coating but little or no evidence of local removal of the protective ZrO_2 film or of 17 - 4 PH transfer.

Nut M-26, torqued to 176° with a Cr-plated 17 - 4 PH washer, had a scratch which extended 180° starting near the middle of the nut face and spiralling inward to the inside edge. Twenty regions were examined on the nut contact surface with the EMP and several spots located in the scratch showed evidence of 17 - 4 PH transfer. Energy dispersive analyses, illustrated in Figure E-2, indicated that the material transferred included particles from the Cr plating and from the 17 - 4 PH substrate.

The washer associated with nut M-26 was edge-mounted, ground through three planes and metallographically examined for Cr plating thickness, uniformity and integrity. In examining the middle plane through the washer diameter, a raised overlap was observed at the inside edge. The overlap appeared to be a machining defect consisting of a burr that had been bent over instead of being cut off during the operation used to deburr the inside edge.

Close examination revealed that the overlapped burr top surface had been plated with Cr and had a height above the washer face of about 0.8 mil. At 7X the overlap appeared as a slight surface irregularity (Figures E-3A and E-3B)

but was readily visible in cross section at 500X (Figure E-3C). It is likely that the overlap, together with the higher angle of rotation (176°), caused the scratch and ensuing 17 - 4 PH transfer to the nut face.

The Cr-plated washers used in this test were pre-production type intended for qualification of tools and training in assembly techniques and thus did not receive the normal liquid penetrant inspection which would have detected the overlap and rejected the washer. Further, the Cr-plating thickness, while appreciably higher than that on the Cr-plated Inconel washers (Table E-I), was not uniform -- ranging from 0.03 - 0.15 mils. The thinner plate thickness was observed at the washer inner hole.

EMP analyses were repeated with a Cr-plated washer from a core production lot. Nut M-29 was torqued once using Neolube lubricant, and the final torque rotation was 100 degrees. The results are also listed in Table E-II. Extensive EMP examination (57 spots) of the nut contact surface showed Cr from the plating but no evidence of 17 - 4 PH transfer. Some 300-type stainless steel contaminant particles were found at the O.D. edge of the nut but were not distributed over the bearing surface itself. Similar contaminants were detected on the bearing surface of a nut torqued with a Cr-plated Inconel washer (Table E-I) and are attributed to assembly tools used during the training of assembly personnel.

TABLE E-1
EMP Analyses of Medium Diameter Nuts Torqued with Thin Cr-Plated Washers

<u>Nut Identity</u>	<u>Neolubed</u>		<u>Torque Cycles</u>	<u>Washer Material</u>	<u>Cr-Plating Thickness (mil)</u>	<u>Cr Transfer</u>	<u>Ni Transfer</u>	<u>Comments</u>
I-1	0	1	Inconel-600		0.04	Yes	Yes	Inconel transfer
I-2	0	2	Inconel-600		0.05	Yes	Yes	Inconel transfer
SS-1	0	1	304 Stainless		0.05	Yes steel transfer	No	Minimal stainless
I-18	1	1	Inconel-600		0.04	Yes detected, but film integrity maintained	Yes ZrO ₂	Inconel particles
I-25	1	2	Inconel-600		0.04	Yes	Yes	Inconel transfer

TABLE E-II
EMP Analyses of Medium Diameter Nuts Torqued Once with Neolubed 17 - 4 PH Washers

Nut Identity	Final Rotation (Degrees)	Cr-Plating Thickness (mil)	EMP Examination				Comment
			Cr Transfer	Fe Transfer	Ni Transfer	Cu Transfer	
M-30	100	bare washer	Yes	Yes	Yes	Yes	17 - 4 PH* transfer
M-25	90	0.08-0.15	Yes	Yes	Yes	Yes	17 - 4 PH detected, but ZrO ₂ film integrity maintained
M-26	176	0.08-0.15	Yes	Yes	Yes	Yes	17 - 4 PH* transfer
M-29	100	0.08-0.25	Yes	Yes	Yes	No	no 17 - 4 PH transfer; some stainless steel contamination

*17 - 4 PH: 16.7 w/o Cr/4.6 w/o Ni/3.5 w/o Cu/balance Fe

Figure E-1

A. Electron Image of Area #1,
Sample I-1 330X

B. Chromium X-Ray Image of Same Area as A 330X

C. Nickel X-Ray Image of Same Area as A 330X

D. Top: High Nickel Inclusion, Area #1 Sample I-1
Bottom: Inconel-600

Electron Microprobe Scans of Sample I-1

Figure E-2

Chromium X-Ray Image 333X

Chromium from the plating

17 - 4 PH transfer

Figure E-3

A. Nut Side 7X

B. Inconel Plate Side 7X

C. Nut Side 500X

Cr-Plated 17 - 4 PH Washer Torqued with Nut M-26

APPENDIX F

CHROMIUM-PLATED WASHER DETAILS

I. Chromium Plating Procedure

Class 2 plating, also known as "industrial chromium" or "hard chromium" was applied to the 17 - 4 PH washers. The bare washers were first electro-cleaned with current using alkaline cleaner at $180 \pm 20^{\circ}\text{F}$. Cathodic cleaning, 22-50 amperes/ft², is used on nickel-containing alloys. The washers were rinsed in clean running water for 1 - 3 minutes and then acid cleaned in a sulfuric acid (40% by volume) and water bath at room temperature for 1 - 15 minutes, i.e., only long enough to remove surface oxides. After being rinsed in running water at room temperature for 1 - 3 minutes, the cleaned washers were prepared for plating by dipping in a standard hardchrome chromic acid - sulfuric acid solution with the CrO_3/SO_4 ratio at 100:1 between $85 - 100^{\circ}\text{F}$. After removal from the dip tank, the washers were plated in a standard hardchrome solution, again with the CrO_3/SO_4 ratio at 100:1, between $125 - 130^{\circ}\text{F}$. After plating the washers were rinsed twice in clean running water at room temperature to ensure removal of all chromic acid. The plated washers were dried with forced clean air blasts and lint-free cloths to avoid water spots. The dried washers were baked for 3 hours at $375 \pm 25^{\circ}\text{F}$ to provide embrittlement relief by removing hydrogen.

II. Chromium-Plated Washer Evaluation

The washers torqued with the medium diameter nuts discussed in Section III.D.3 were edge-mounted, ground through several planes and metallographically examined at each stage for chromium plating thickness, uniformity and integrity. In all cases the chromium plating was thicker at the washer periphery than along the flat contact surfaces. All of the washers had ≥ 0.2 mil Cr coating thickness on their contact surfaces. The washers from fastener M-21 and X-5 are shown in Figures F-1A and F-1B. No cracks or breaks were observed in the torqued contact chromium coating.

Microhardness measurements were performed on the bare 17 - 4 PH washer matrix and on 0.4 mil and 0.6 mil thick Cr-plated 17 - 4 PH samples from lot 11M (Figure F-1C) and 11D (Figure F-1D). Knoop hardness values, obtained with a 100 gram load, are listed in Table F-I. Overall average Knoop hardness numbers of 391 and 367, corresponding to about 38 and 35 Rockwell "C", were obtained for the 0.4 - 0.6 mil thick Cr plating and the aged 17 - 4 PH washers, respectively. These values are about double the 215 Knoop number (90 Rockwell "B") for Zircaloy. Thus, the chromium serves as a wear-resistant surface which prevents transfer, smearing and galling by the underlying 17 - 4 PH washer alloy. Since Inconel-600 has about the same hardness (87 Rockwell "B") as Zircaloy, smearing and bonding can more readily occur. Further, if flaking or local removal of the Cr plating should occur during fastener assembly, the relatively high hardness of 17 - 4 PH, about a factor of 1.7 above that of Zircaloy, plus its relatively low nickel content (4.6 w/o) and the presence of the ZrO_2 film on the Zircaloy nut, would combine to minimize smearing and any subsequent accelerated hydriding. This is consistent with the hydriding data on fasteners assembled with bare 17 - 4 PH washers (Section III-D).

TABLE F-I

Knoop Hardness ValuesChromium Plating

<u>Lot 11M</u>	<u>Lot 11D</u>	<u>17 - 4 PH</u>
390	382	363
364	317	368
395	415	358
382	415	374
445	408	370

Figure F-1

17 - 4 PH
↓Cr
↓17 - 4 PH
↓Cr
↓

A. Lot 11A

0.2 mil

B. Lot 11E

0.3 mil

↑
17 - 4 PH↑
Cr

C. Lot 11M

0.4 mil

↑
17 - 4 PH↑
Cr

D. Lot 11D

0.6 mil

APPENDIX G

A MODEL FOR THE ANALYSIS OF HYDRIDING IN NICKEL-SMEARED ZIRCALOY*

I. BACKGROUND

Certain core assembly operations, such as bolting a corrosion filmed Zircaloy fastener to an Inconel support, results in intimate Zircaloy/Inconel contact. In addition the torquing may seriously damage or remove some of the protective ZrO_2 film where the Zircaloy surface is in contact with the Inconel. Smearing and bonding of Inconel onto local regions of the mating Zircaloy contact surface can then occur. This inhibits re-formation of the zirconium oxide barrier, allowing accelerated hydriding of the Zircaloy. The experimental results of this report have shown that under such conditions Inconel bonded to Zircaloy can act as a window through which hydrogen from the aqueous coolant diffuses rapidly into the underlying Zircaloy. Evidently the hydrogen potential across the Inconel is sufficient to cause the immediate formation of a zirconium hydride phase at the Zircaloy/Inconel interface. The phenomenon is illustrated in Figure G-1.

II. ANALYSIS

The mechanism of hydriding of an oxide-free zirconium surface has been analyzed in terms of diffusion processes (Reference G-1). In the present work the diffusion path for the hydrogen is through the nickel alloy into the bare Zircaloy. The rate controlling step is the diffusion of hydrogen through that compound with the lowest diffusivity for H_2 . In addition to dissolving in α -zirconium, hydrogen reacts with zirconium to form several hydride phases, an epsilon, delta and a metastable gamma hydride (Reference G-2). Wagner has discussed the general problem of diffusion in binary systems of more than one phase (Reference G-3). Gulbransen and Andrew have applied Wagner's treatment to the hydriding of zirconium (Reference G-1).

*Developed by Dr. G.P. Marino (formerly at the Bettis Laboratory, presently with the Department of Energy - Nuclear Regulatory Commission)

The model used is shown schematically in Figure G-2. The hydride rim thickness, X , in cm, is related to the diffusivity of hydrogen through zirconium hydride by the equation:

$$X = 2\gamma\sqrt{D_{II}t} \quad (G-1)$$

where D_{II} is the diffusion coefficient of hydrogen in the δ and ϵ hydride phases (cm^2/sec); t is the diffusion time (sec.); γ is a dimensionless

parameter which is a function of the concentration ratio $\frac{C_s - C_{II, I}}{C_{II, I} - C_0}$

at the temperature of interest.

Table G-1 lists values for γ , $\text{ERF}(\gamma)$ and the calculated values of the concentration ratio. Figure G-3 is a graph of the data of Table G-1 where γ is plotted against the concentration ratio. Some sample concentration calculations are illustrated in Table G-2. For example, if ϵ -hydride is

present at the Inconel - hydride interface,

$$\frac{C_s - C_{II, I}}{C_{II, I} - C_0} = \frac{21,620 - 15,230}{15,230 - 25} = 0.420$$

which yields from Figure G-3, $\gamma = 0.42$. If only δ -hydride is present,

$$\frac{C_s - C_{II, I}}{C_{II, I} - C_0} = \frac{16,940 - 15,230}{15,230 - 25} = 0.122 \text{ and } \gamma = 0.22.$$

Hydrogen diffusion in zirconium hydride has been measured over the 400° - 1200°F temperature range (Reference G-4) and the data expressed as:

$$D_{II} = 0.1 e^{-20,700/RT} \quad (G-2)$$

At 450°F, $D_{II} = 4.48 \times 10^{-10} \text{ cm}^2/\text{sec}$. At 520°F, $D_{II} = 1.95 \times 10^{-9} \text{ cm}^2/\text{sec}$. The diffusion coefficients for hydrogen in Zircaloy-4 are 1.81×10^{-7} and $3.88 \times 10^{-7} \text{ cm}^2/\text{sec}$ at 450°F and 520°F, respectively (Reference G-5). This illustrates that hydrogen diffusion in the hydride phase is several hundred times slower than in α -Zircaloy.

The diffusion model neglects the effects of thermal gradients and supercharging. The phenomenon of supercharging has been discussed by Marino (Reference G-6). Supercharging is the ability of hydrogen saturated Zircaloy to pick up hydrogen essentially directly into its volume (where it precipitates as delta-hydride) without forming and growing a hydride rim at the entry location. This is very different from the typical reaction (such as oxidation) where further additions of a reactant cause immediate growth of the second phase at the metal surface. Supercharging is due to (1) the ability of Zircaloy to become supersaturated with hydrogen, (2) the large diffusion coefficient of hydrogen in Zircaloy, and (3) the hydrogen ingress rate (flux) at the Zircaloy surface. Thus, slowly entering hydrogen at the surface supersaturates the surface (thereby causing a concentration gradient) and is able to diffuse deeper into the volume where it eventually precipitates at favorable sites (grain boundaries for example) as the delta-phase. This is critically dependent upon the ingress rate (J_0 , in gms H/cm²/sec.). If J_0 is too high, the excess hydrogen cannot diffuse away prior to precipitation at the surface with the formation of a hydride rim. Accelerated corrosion experiments in concentrated LiOH show supercharging and no hydride rims (Reference G-7). In these experiments J_0 was $\sim 3 \times 10^{-10}$ gms H/cm²/sec at 570°F, indicating that J_0 must exceed these values for Zirconium hydride rims to form and keep growing. Also, if a hydride rim does form and grows via equation G-1, a limiting thickness will be reached at which J_0 falls below the critical value (J_c) needed for rim formation. This is seen by differentiating equation G-1 with respect to time:

$$\frac{dX}{dt} = \gamma \sqrt{\frac{D}{t}} \quad (G-3)$$

The rate of rim growth (dX/dt), and also J_0 , decreases as the time increases, or equivalently as the rim thickens.

The next step is to determine the critical flux (J_c) below which no further rim growth occurs. When related to equation G-1, the maximum rim thickness can then be estimated for any temperature. Erickson (Reference G-8) has determined and plotted the equilibrium partial pressures of hydrogen gas over the delta and epsilon phases of Zirconium hydride. Interpolation from his plots yields:

$$\log_{10} p_{H_2}^{\delta} = \frac{-7916.7}{T} + 8.225 \text{ mm Hg} \quad (G-4a)$$

$$p_{H_2}^{\delta} = 1.68 \times 10^8 e^{-18,232/T} \text{ mm Hg} \quad (G-4b)$$

Using the conversion factor

$$\frac{(1.013 \times 10^6)}{760}, \text{ gives}$$

$$p_{H_2}^{\delta} = 2.24 \times 10^{11} e^{-18,232/T} \text{ dynes/cm}^2 \quad (G-4c)$$

For the epsilon hydride:

$$\log_{10} p_{H_2}^{\epsilon} = \frac{-9765.5}{T} + 11.82 \text{ mm Hg} \quad (G-5)$$

These equations state that any hydrogen gas pressure exceeding that given will cause the immediate formation of δ or ϵ -hydride on a bare, i.e., oxide-free, Zr surface at the absolute temperature T.

The effect of the hydrogen partial pressure can be translated into the impingement rate (I.R.) of hydrogen gas molecules striking the Zr surface via the kinetic theory of gases. Thus

$$J_c = \text{I.R.} = p_{H_2} \frac{\text{molecules of } H_2}{(2\pi mkT)^{1/2} \text{ cm}^2 \cdot \text{sec}} \quad (G-6)$$

where

m is the mass of the hydrogen molecule, and

$$m = \frac{2.0194}{6.02252 \times 10^{23}} = 3.353 \times 10^{-24} \text{ g}$$

k is Boltzmann's constant, and

$$k = 1.38054 \times 10^{-16} \text{ dyne} \cdot \text{cm}/^\circ\text{K}$$

and T is the absolute temperature, $^\circ\text{F}$

This assumes that the impingement rate equals the hydrogen absorption rate, and allows the use of the kinetic theory of gases, and existing thermodynamic data, to calculate the critical hydrogen ingress rate for hydride rim growth.

Inserting the equation for the pressure of hydrogen gas above the delta hydride phase (G-4c) and multiplying by 3.353×10^{-24} to convert molecules to grams, gives:

$$J_c = \frac{1.39 \times 10^7 e^{-18,232/T}}{\sqrt{T}} \text{ gms H/cm}^2/\text{sec} \quad (\text{G-7})$$

This equation gives an equilibrium value, but Zr can supersaturate with hydrogen before precipitation takes place. The experimental measurements (References G-8 and G-9) are in terms of solubilities, which can be converted, using Sievert's law (Reference G-10), to partial pressures. The hydrogen concentrations are:

$$C_{eq} = K \sqrt{P_{H_2}}^{eq} \text{ for equilibrium, and}$$

$$C^* = K \sqrt{P_{H_2}^*} \text{ for supersaturation before } \delta\text{-formation}$$

Thus

$$P_{H_2}^* = P_{H_2}^{eq} \left(\frac{C^*}{C_{eq}} \right)^2$$

Using Kearns' measurements (Reference G-9),

$$C^* = 3.10 \times 10^5 e^{-9115/RT}$$

$$C_{eq} = 9.90 \times 10^4 e^{-8250/RT}, \text{ and}$$

$$\left(\frac{C^*}{C_{eq}} \right)^2 = 9.805 e^{-870.7/T}$$

$$\text{Now, } J_c^* = J_c \times 9.805 e^{-870.7/T}, \text{ and}$$

$$J_c^* = \frac{1.36 \times 10^8 e^{-19,103/T}}{\sqrt{T}} \quad (G-8)$$

This yields J_c^* values of 2.34×10^{-10} and 3.36×10^{-9} gms H/cm²/sec at 450 and 520°F, respectively. These estimates are in reasonable accord with the suspected critical flux ($> 10^{-10}$ gms H/cm²/sec). Also equation (G-8) indicates that the critical flux needed to form a hydride rim increases as the temperature increases.

If the rim at the Zr-hydride interface is growing at dx/dt (Equation G-3), the flux (J_0) must be such that:

$$J_0 \cdot A \cdot dt = dx \cdot A \cdot (C_\delta - C_\alpha) \text{ for mass balance}$$

where

A = area of the interface

C_δ = concentration (8.61×10^{-2} gms H/cc) of δ ZrH_{1.5}

C_α = concentration ($3.1 \times 10^5 e^{-9115/RT}$) g of hydrogen/cc of α - Zircaloy

Since $C_\delta \gg C_\alpha$, at 450° and 520°F,

$$J_0 = \frac{dXC_s}{dt} = 8.61 \times 10^{-2} \gamma \sqrt{\frac{D_{II}}{t}} \quad (G-10)$$

Equating J_0 (G-10) and J_c^* (G-8) yields:

$$t_s = \frac{(8.61 \times 10^{-2})^2 \gamma^2 D_{II} T e^{38,206/T}}{(1.36 \times 10^8)^2} \quad (G-11)$$

where t_s is the time in seconds for the rim to stop growing and supercharging to predominate. To obtain the rim thickness at which this occurs, take the square root of equation (G-11) and insert into equation (G-1).

Thus,

$$X_m = \frac{0.172 \gamma^2 D_{II} T^{1/2} e^{19,103/T}}{1.36 \times 10^8} \text{ cm} \quad (\text{G-12})$$

Using Vetrano's diffusion data (Reference G-4) and the 0.22 γ value for delta-hydride, the equations are:

$$X_m = 2.44 \times 10^{-11} T^{1/2} e^{8685/T} \text{ cm} \quad (\text{G-13})$$

for the maximum rim thickness at temperature T, and

$$t_s = 7.71 \times 10^{-20} T e^{27,788/T} \text{ seconds} \quad (\text{G-14})$$

for the time required to reach X_m . Note that X_m increases as T decreases. Larger maximum hydride rims are predicted at lower temperatures even though the growth rate [Equation (G-3)] decreases with temperature. The reason for this effect is that at lower temperature, lower values of J^*_c are required for hydride rims to form [Equation (G-8)], thus allowing the rim to grow to a much larger size. These predictions are consistent with the experimental data of this report.

III. LIMITATIONS

A. Uncertainties

1. The measurements of the diffusion of hydrogen in the zirconium hydrides, reported in the literature, vary over several orders of magnitude.
2. The hydride phase (δ or ϵ) formed governs the value of γ and the rim growth rate.
3. There is no way of confirming the J^*_c estimate.

B. Assumptions

1. The analysis is for one dimension only. Where the oxide is removed over small spots, then the hydride rim would grow outwardly in the radial and circumferential directions as well as axially. Such a dispersion would tend to diminish the axial rim depth to approximately one-third (assuming isotropy).

2. The model assumes that the hydride rim remains intact. However, cracking and spalling have been observed in some of the tests.

3. No account has been taken of the effect of thermal gradients. However, such gradients probably did not exist to any great extent in the fastener components tested.

4. It has been assumed that damage to the Zircaloy surface completely removes the oxide film. If such is not the case, e.g., the oxide thickness is reduced by a factor of 10 but a thin layer remains, then accelerated hydriding could take place but no hydride rims need form. In agreement with this, Zircaloy samples exhibiting considerable accelerated hydriding but no hydride rims have been observed. Thin zirconium oxide films can reduce the hydrogen ingress rate below the critical value (J^*_c) (Reference G-11).

IV. SUMMARY

An analytical model was developed to predict hydride rim formation at nickel alloy - smeared Zircaloy surfaces. The analysis indicates that the initial hydrogen ingress into the nickel smeared Zircaloy surface is greater than the temperature-dependent critical hydrogen flux needed to form a hydride rim, and the delta hydride phase precipitates immediately. Since the hydrogen ingress rate at the surface is greater than its rate of diffusion away from the surface due to the low diffusivity of hydrogen in the hydride phase, the rim grows in thickness. The rate of rim growth decreases with the square root of time until the rim builds up to a limiting size. Continued hydrogen ingress can then increase the hydrogen content of the Zircaloy specimen by supercharging.

V. REFERENCES

- G-1 E.A. Gulbransen and K.F. Andrew, "Diffusion of Hydrogen and Deuterium in High Purity Zirconium", J. Electrochem. Soc., 101, 560-66 (1954).
- G-2 W.M. Mueller, J.P. Blackledge and G.G. Libowitz, "Metal Hydrides", Academic Press, NY, 1968, pp. 242-78.
- G-3 C. Wagner, quoted by W. Jost, "Diffusion in Solids, Liquids and Gases", Academic Press, Inc., NY, Revised Edition, 1960, pp. 69-72.
- G-4 J.B. Vetrano, et al, "Migration of Hydrogen in Zirconium Hydride," BMI-1259, March 1958; BMI-1267, May 1958.
- G-5 J.J. Kearns, "Diffusion Coefficients of Hydrogen in α -Zirconium, Zircaloy-2 and Zircaloy-4", J. Nucl. Material, 43, 330-3 (1972).
- G-6 G.P. Marino, "Hydrogen Supercharging in Zircaloy", Mater. Sci. Eng., 7, 335-41 (1971).
- G-7 R.A. Murgatroyd and J. Winton, "Hydriding Zircaloy-2 in Lithium Hydroxide Solutions", J. Nucl. Mater., 23, 249-56 (1967).
- G-8 W.H. Erickson, "Hydrogen Solubility in Zirconium Alloys," J. Electrochem. Techn., 4, 205-11 (1966).
- G-9 J.J. Kearns, "Terminal Solubility and Partitioning of Hydrogen in the Alpha Phase of Zirconium, Zircaloy-2 and Zircaloy-4", J. Nucl. Mater., 22, 292-303 (1967).

- G-10 L. S. Darken and R.W. Gurry, "Physical Chemistry of Metals", McGraw-Hill, NY, 1953, p. 132, 258.
- G-11 T. Smith, "Kinetics and Mechanism of Hydrogen Permeation of Oxide Films on Zirconium," J. Nucl. Mater., 18, 323-36 (1966).

TABLE G-1

GAMMA, ERROR FUNCTION OF GAMMA, AND
CALCULATED VALUES OF $C_s - C_{II,I}/C_{II,I} - C_o$

GAMMA	ERF (Gamma)	$C_s - C_{II,I}$
		$C_{II,I} - C_o$
0.00	0.0000	0.000
0.03	0.0282	0.001
0.05	0.0564	0.005
0.10	0.1125	0.020
0.15	0.1680	0.046
0.20	0.2227	0.082
0.25	0.2763	0.130
0.30	0.3286	0.191
0.35	0.3794	0.266
0.40	0.4284	0.356
0.45	0.4755	0.464
0.50	0.5205	0.592
0.55	0.6533	0.743
0.60	0.6039	0.921
0.65	0.6420	1.129
0.70	0.6778	1.373
0.75	0.7112	1.659
0.80	0.7421	1.996
0.85	0.7707	2.391
0.90	0.7970	2.858
0.95	0.8209	3.408
1.00	0.8427	4.060
1.10	0.8802	5.755
1.20	0.9103	8.172
1.30	0.9340	11.663
1.40	0.9523	16.776
1.50	0.9661	24.370
1.60	0.9763	35.816
1.70	0.9838	53.339
1.80	0.9891	80.575

$$\text{ERF}(\gamma) = \frac{2}{\sqrt{\pi}} \int_0^\gamma \exp(-z^2) dz$$

$$\frac{C_s - C_{II,I}}{C_{II,I} - C_o} = \sqrt{\pi} \gamma e^{\gamma^2} \text{ERF}(\gamma)$$

NOTE: The values of ERF (γ) in increments of γ of 0.0001 can be found in the Mathematical Tables Project, "Table of Probability Functions", Volume 1, Federal Works Agency, Works Project Administration, New York, 1941.

TABLE G-2

HYDROGEN CONCENTRATION CALCULATIONS

I. Case A: ϵ - Zirconium hydride present

C_S = maximum hydrogen content for ϵ -hydride (ZrH_2)

$$\begin{array}{rcl} ZrH_2: & 2 \text{ moles H} & = 2.016 \text{ gms} \\ & 1 \text{ mole Zr} & = \frac{91.22 \text{ gms}}{93.236 \text{ gms}} \end{array}$$

$$w/o \text{ H} = \frac{2.016}{93.236} \times 100 = 2.162 \text{ w/o} = 21,620 \text{ ppm H}$$

$C_{II,I}$ = minimum hydrogen content for δ -hydride ($ZrH_{1.4}$)

$$\begin{array}{rcl} ZrH_{1.4}: & 1.4 \text{ moles H} & = 1.411 \text{ gms} \\ & 1 \text{ mole Zr} & = \frac{91.22 \text{ gms}}{92.631 \text{ gms}} \end{array}$$

$$w/o \text{ H} = \frac{1.411}{92.631} \times 100 = 1.523 \text{ w/o} = 15,230 \text{ ppm H}$$

II. Case B: only δ -zirconium hydride present

C_S = maximum hydrogen content for δ -hydride ($ZrH_{1.56}$)

$$\begin{array}{rcl} ZrH_{1.56}: & 1.56 \text{ moles H} & = 1.572 \text{ gms} \\ & 1 \text{ mole Zr} & = \frac{91.22 \text{ gms}}{92.792 \text{ gms}} \end{array}$$

$$w/o \text{ H} = \frac{1.572}{92.792} \times 100 = 1.694 \text{ w/o} = 16,940 \text{ ppm H}$$

$C_{II,I}$ = minimum hydrogen content for δ - hydride ($ZrH_{1.4}$) = 15,230 ppm H

C_0 = average as-built concentration of hydrogen in as-fabricated Zircaloy
= 25 ppm.

ZIRCONIUM HYDRIDE RIM FORMATION

FIGURE G-1
Zirconium Hydride Rim Formation

C_s IS THE CONCENTRATION OF HYDROGEN IN THE HYDRIDE AT THE INCONEL - HYDRIDE INTERFACE

$C_{II,I}$ IS THE CONCENTRATION OF HYDROGEN IN THE HYDRIDE AT THE HYDRIDE - ZIRCALLOY INTERFACE GIVEN BY THE EQUILIBRIUM PHASE DIAGRAM IN THE $\alpha + \delta$ REGION AT THE REACTION TEMPERATURE

C_0 IS THE INITIAL NOMINAL HYDROGEN CONTENT OF THE ZIRCALLOY

X IS THE HYDRIDE RIM THICKNESS

FIGURE G-2
DIFFUSION OF HYDROGEN IN ZIRCALLOY

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FIGURE G-3
GAMMA VS. CONCENTRATION RATIO