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FRACTURE BEHAVIOR AND MICROSTRUCTURAL CHARACTERISTICS OF IRRADIATED ZIRCALOY CLADDING*

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ABSTRACT

Zircaloy cladding tube specimens from commercial power reactor fuel assemblies (burnup >22 MWd/kgU) have been deformed to fracture at 325°C by either the internal gas-pressurization or the expanding-mandrel technique in helium or argon environment containing no fission product species (e.g., I, Cs, or Cd). The fracture surfaces of 11 irradiated specimens fractured by internal gas pressurization were examined by scanning electron microscopy, and 7 specimens were found to contain various degrees of the pseudocleavage feature that is characteristic of pellet-cladding interaction failures. Out of 10 test specimens fractured by expanding-mandrel loading, 5 were found to contain regions of pseudocleavage on the fracture surfaces. The specimens exhibited "X-marks" on the outer surface and brittle incipient cracks distributed on the inner surface, which are also characteristic of pellet-cladding interaction failures. Transmission/high-voltage electron microscopy examinations of the thin-foil specimens obtained from regions adjacent to the failure sites showed that the ductile-failure specimens were characterized by a high density of dislocations which showed normal $\vec{a}$ -type Burgers vectors. In contrast, the brittle-type specimens were characterized by comparatively few dislocations which formed substructures. The dislocations in the brittle

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specimens were decorated by Zr_3O precipitates 2-6 nm in size, and cubic- ZrO_2 precipitates ≤ 10 nm in size were also observed in association with most of the dislocation substructures. These observations indicate a general immobilization of the dislocations. The low-ductility brittle-type failures appear to have been produced primarily as a result of the Zr_3O and cubic- ZrO_2 precipitates, augmented by precipitates of bulk hydride 35-100 nm in size. The bulk nature of these precipitates, which contrasts with the surficial nature of monoclinic ZrO_2 and χ -hydride precipitates, was discerned by " $^{2\frac{1}{2}}D$ -microscopy" of weak-beam dark-field images. In-situ irradiation of the spent-fuel cladding specimens by 1-MeV electrons at 325°C indicates that the Zr_3O and cubic- ZrO_2 precipitation is irradiation-induced whereas the bulk hydride is not.

INTRODUCTION

The Zircaloy cladding of water reactor fuel rods is susceptible to low-ductility brittle-type failure, commonly known as pellet-cladding interaction (PCI) failure. A PCI failure is usually characterized by low failure strain with negligible wall thinning, branching brittle cracks, "X-marks" on the outer surface, and a fractographic feature commonly termed as either "pseudo-" or "quasi-cleavage". Since the early discoveries of iodine-induced stress corrosion cracking (SCC) [1] and Cd-induced liquid-metal embrittlement (LME) [2] in unirradiated Zircaloys, PCI failure has been largely associated with the influence of fission product species (e.g., I, Cd, Cs, CsI, ZrI_4), which implies either an SCC or LME mechanism for the failure. The implication is primarily based on the similarities between the fractographic and macroscopic failure characteristics [3] of reactor fuel cladding and specimens from simulation tests. Implicitly assumed in this argument is that those

characteristics are not only generally valid but also sufficient to establish a PCI failure mechanism. However, no characteristics based on transmission electron microscopy (TEM) have been reported. The availability of the SCC-inducing species in amounts sufficient to cause a brittle-type failure in reactor has been reexamined and tested in a number of recent publications [4-6] in relation to the complex interplay of chemical reactions among fission products and the radiolytic effects of fission fragments. The results show that the fission products I and Cs form the compound CsI, which is not an SCC-inducing agent, and that irradiation with fission fragments does not break up the compound to release I, which would cause brittle SCC failures. The results, therefore, stimulate a careful reexamination of the phenomenon from a wider perspective.

Although the majority of mechanistic studies have been conducted in environments containing some kind of fission product species to induce brittle-type failures, brittle-type fracture surface morphologies have also been observed in simulation tests on unirradiated Zircalloys [7-10] and Zr-2.5% Nb [11] in air [7,8,11] or in air after oxidation [9,10]. Brittle-type morphologies have been observed after deformation in air at slow strain rates at 300-330°, conditions for which Zr- and Ti-base alloys have been known to exhibit a ductility minimum [7,8]. Since no fission product species were involved in the tests, the observations have been addressed by other investigators [12,13]. However, the observed behaviors [7,8,11] remain essentially unexplained. Low-ductility brittle failures have also been reported [14,15] for irradiated Zircalloys deformed and fractured in the absence of fission product species. The observations of brittle cracks reported by Bergenlid et al. [16] after fast (total hold time 0.16-1.1 min) power ramping in a test reactor, as well as those described by Bain et al. [17], are believed to be

significant in that these hold times are simply too short to permit transport of the fission product species in the Zircaloy material. These observations suggest an irradiation-induced general embrittlement rather than the SCC or LME process.

In view of this background, it appears timely to reexamine the fundamental deformation and fracture mechanism (in the absence of any fission product species) for those Zircaloy materials that would be most relevant to an actual PCI failure. The best material would undoubtedly be high-burnup spent-fuel cladding discharged from a commercial power reactor. High-burnup spent-fuel cladding is characterized by localized stresses, high-density radiation-induced defects, mechanical constraints imposed by pellet-cladding friction, microstructural and compositional changes (e.g., O and H uptake from in-service corrosion), and geometrical changes due to creep and bowing. It has been well established in the literature that the deformation and fracture behavior of Zr-base alloys can be influenced by synergistic effects involving more than one of the above factors, e.g., strain aging [18-20] and radiation-anneal hardening [21-23]. These phenomena are most pronounced in the temperature range 300-350°C and are commonly accepted to be associated with oxygen interstitials which interact with either dislocations or irradiation-induced defects. Although the potential significance has not been recognized, there have been circumstantial indications reported in the literature that the interaction between the irradiation-induced defects and nonmetallic elements appears to play an important role in deformation of Zr-base alloys [24-27]. Such interactions, as well as the phenomenon of radiation-induced precipitation, have been reported for other alloy systems (e.g., see Ref. 28). However, the roles of similar effects in Zircaloys had not been recognized until very recently when the observation of Zr_3O precipitates was reported in

association with fracture properties of irradiated Zircaloy [29-31]. Our primary objectives in this work are then twofold, namely, (1) to determine comparative ductile-brittle fracture behavior of high-burnup fuel cladding under expanding-mandrel and internal gas-pressurization loading conditions in a controlled atmosphere not containing any fission product species, and (2) to elucidate the fracture mechanism(s) through a correlation of the failure behavior with microstructural characteristics.

EXPERIMENTAL PROCEDURE

Spent-Fuel Cladding

Spent-fuel cladding sections were obtained from two operating commercial reactors, i.e., the Big Rock Point (boiling-water) and H. B. Robinson (pressurized-water) reactors. The fuel burnup and neutron fluence were in the range of 22-28 MWd/kgU and $3.3-4.4 \times 10^{21}$ n/cm² ($E > 0.1$ MeV), respectively. The cladding sections were obtained from unfailed fuel rods. Before the sections were cut, they were inspected by the pulsed eddy-current technique to ensure that no defects existed. The as-fabricated archive materials exhibited the typical crystallographic texture of commercial fuel cladding, with the basal poles oriented $\sim 30^\circ$ on each side of the radial direction toward the tangential direction. The cladding material was typically $\sim 70\%$ cold worked and stress-relieved. As a result of the stress-relief treatment, the material was partially recrystallized. Dislocations normally observed in the stress-relieved archive material were annealed out during the in-reactor service.

Specimen Geometry and Preparation

Specimens for the internal gas-pressurization and expanding-mandrel tests were cut into lengths of ~ 152 and ~ 50 mm, respectively. The outside diameter and wall thickness of the Big Rock Point cladding specimens were 14.28 and

1.29 mm, respectively. Similar dimensions for the H. B. Robinson cladding were 10.70 and 0.61 mm, respectively.

After removal of the fuel, the inside surface of each specimen was nylon-brushed to remove small fuel particles, and the entire specimen was ultrasonically cleaned in alcohol. For the expanding-mandrel loading tests, dilute HNO_3 and H_2O_2 solutions were used successively after the mechanical brushing to clean the inner surface of the specimen. Then the entire specimen was again cleaned ultrasonically in alcohol. The extra cleaning procedure was necessary to reduce the alpha radiation level before the specimens were transferred to a low-level hot cell for the mandrel-loading tests.

Internal Gas-Pressurization Tests

The hot-cell facility and procedures for conducting the helium-pressurization tests of the irradiated cladding were similar to those reported by Yaggee et al. [32]. However, unlike the specimen preparation described in Ref. 32, the specimens in the present fracture tests were mechanically sealed with a modified "Swagelok" connector at room temperature without any prior annealing of the ends. An entirely new gas-handling and gas-pressurization system, which had not been exposed to any fission product species, was assembled for the present tests. The system was connected to a pressurized cylinder of research-grade helium and put into a hot cell for operation. No fission product species were introduced into the system. The helium-pressurized test specimen was then sealed off from the atmosphere in a stainless steel cylinder. Research-grade argon, pressurized to ~20% above atmospheric pressure, was continuously flowed at a rate of ~0.01 l/s through the gap between the stainless steel cylinder and the specimen tube. The steel cylinder itself was contained in a temperature-controlled furnace. In this way, the argon atmosphere bounded by the outer surface of the specimen and the

inner surface of the stainless steel cylinder was maintained at a purity similar to that of the research-grade argon. Results of starch-solution tests of the specimen outer-surface environment (at 325°C) were identical with those of tests of a gas flowing from an isolated argon tank (at room temperature) and showed no signs of iodine. Examination of oxide layer thicknesses on the outer and inner surfaces of the specimen before and after the fracture tests at 292-325°C did not show any indication of extra oxidation during these tests.

Expanding-Mandrel Tests

Fracture tests were conducted at 292-325°C by means of an expanding-mandrel loading technique in a low-level hot cell [33]. Loading of the 50-mm-long specimens was achieved by an expanding internal mandrel, which is shown schematically in Fig. 1. The hardened-steel tapered mandrel fit within an expanding sleeve with a matching taper. The sleeve was surrounded by either split hollow ceramic cylinders to simulate cracked UO_2 fuel, or a thin split W-Re alloy ring to simulate the stress concentration at a pellet-pellet interface. Slow diametral strain rates were achieved by axial compression of the mandrel assembly in an Instron machine at controlled crosshead displacement rates. The mandrel assembly was fixed vertically on the bottom pedestal of the Instron machine. A concentric quartz cylinder, fixed in a groove made in the bottom pedestal, surrounded the mandrel. The annulus between the mandrel assembly and the quartz cylinder was then purged with argon several times before the specimen was heated with a furnace. An environment of flowing argon (~ 3.3 l/s) of 99.99% purity at slightly higher than atmospheric pressure was maintained in the annulus during a test. No fission product species were added to the system or to the carefully cleaned specimen.

Fig. 1. Schematic of expanding-mandrel assembly used to fracture Zircaloy spent-fuel cladding under simulated pellet-cladding interaction conditions in a flowing argon environment.

Initially, each specimen was deformed at a constant diametral expansion rate (i.e., constant arbor displacement rate), which was used to calculate the diametral strain rate during transient loading. After the transient loading, the specimen deformed under a constant maximum load. Ductile failure of the specimen could be detected by an abrupt decrease in mandrel load which was recorded as a function of arbor displacement and time [33]. However, for brittle-type pinhole failures, detection of the exact moment of throughwall failure was not possible since no sudden drop of mandrel load was noticed. As a result, the mandrel displacement and the ring expansion continued even after a failure occurred. Consequently, the failure diametral strains of those tests could not be determined. The diametral strain measured after termination of a test, therefore, indicates only an upper limit of the failure strain, which would be somewhat smaller than the measured value.

Some of the expanding-mandrel tests were conducted on specimens constrained in the axial direction. The axial constraint was provided by a specially designed specimen constraint fixture [34]. The vertically split fixture encloses the 50-mm-long specimen and provides axial constraint by securing the ends of the specimen with 2.14-mm-diameter Inconel pins. The pins extend through the specimen wall to within 0.2 mm of the inner surface. Typical post-test measurements established no detectable decrease in specimen length or ovalization of the holes.

Post-Test Examination

Procedures for post-test examinations by optical microscopy, scanning electron microscopy (SEM), TEM, and high-voltage electron microscopy have been described elsewhere [30]. A 20-mm-long "clamshell" was cut from the specimen section that contained an identified or suspected throughwall failure site. Outer and inner surfaces of the clamshell were then examined by SEM to

determine patterns of crack distribution. Subsequently, specimens for SEM fractography, TEM, and optical microscopy were prepared according to the procedure described in Ref. 30. The TEM disks were jet-thinned in electrolyte solutions of perchloric acid, butylcellosolve, and methanol (volume ratio 2:12:30) maintained at -70°C . The foil plane of the TEM specimen was nearly perpendicular to the cladding radial direction. The thin-foil specimens were then examined in a JEOL CX-II or in a Kratos/AEI-EM7 high-voltage electron microscope (HVEM), which were operated at 0.1 and 1 MeV, respectively. The latter, equipped with a double-tilt hot stage, has a demonstrated lattice resolution of 0.35 nm. The diffraction patterns obtained from the HVEM are far more accurate than those from the conventional microscopes. The camera lengths of the microscopes were calibrated independently. Reflections from the α -Zr matrix were used as standards to find an exact camera length for each diffraction pattern.

Chemical Analysis

Some of the 3-mm-diameter TEM specimens obtained from regions adjacent to the throughwall failure sites of several specimens were analyzed chemically to determine the local O and H contents. Outer- and inner-surface layers of each disk were mechanically ground and polished to obtain an $\sim 10\text{-}\mu\text{m}$ -thick disk from midwall material, which was subsequently jet-thinned as described above. A typical thin-foil specimen for the chemical analysis weighed $\sim 10\text{ mg}$. O and H contents of the specimens were determined by the inert-gas fusion technique.

RESULTS

Summaries of the internal gas-pressurization and expanding-mandrel test results are given in Tables I and II, respectively. In addition to ductile rupture failures, a number of low-ductility brittle-type failures were

Table I. Summary of internal gas-pressurization stress rupture test results for spent Zircaloy spent-fuel cladding

Specimen number	Reactor	Material	Fuel burnup (MWd/kg U)	Fluence (10^{21} n/cm ² , E > 0.1 MeV)	Test temp. (°C)	Hoop stress		Failure time (h)	Failure diametral strain (%)	Average diametral strain rate (s ⁻¹)	F _p ^a
						MPa	ksi				
165AG10	Big Rock Point ^b	Zircaloy-2	22.4	3.3	325	384	55.6	1.0	1.1	3.0×10^{-6}	0.95
165AE4A					325	344	49.8	25.1	0.8	9.0×10^{-7}	0
165AE4B					325	337	48.8	207.6	0.4	5.4×10^{-9}	0.78
165W-21					325	514	74.5	7.9	1.0	3.5×10^{-7}	0
217A2G	H. B. Robinson ^c	Zircaloy-4	27.7	4.4	292	552	80.1	113.2	11.7	3.0×10^{-7}	0
217B2B					292	545	79.0	108.2	2.5	6.0×10^{-8}	0
217B4B					292	498	72.3	218.5	1.4	2.0×10^{-8}	0.14
217C2B					325	469	68.5	236.7	2.4	3.0×10^{-8}	0.17
217C4B					325	315	45.8	311.6	-	-	0.40
217A4B					325	315	45.8	294.2	-	-	0.12

^aMaximum fraction of wall thickness exhibiting pseudocleavage-plus-fluting features on the fracture surface.

^bOxide layer thickness, 0.5-10 μ m on inner and 50-70 μ m on outer surfaces.

^cOxide layer thickness, 0.5-7 μ m on inner and 20-30 μ m on outer surfaces.

Table II. Summary of expanding-mandrel fracture test results for Zircaloy-4 spent-fuel cladding^a from the H. B. Robinson PWR.

Specimen number	Test temp. (°C)	Time at transient loading (h)	Average strain rate during transient loading (s^{-1})	Maximum mandrel load (kg)	Time under creep mode at max. load (h)	Total time under loading (h)	Final plastic strain at outer surface ^b (%)	Axially constrained	Failure mode	Fracture surface morphology
217A2C	292	17.1	5×10^{-7}	505	0	-	1.2	No	Not failed	-
217A2D	292	5.0	5×10^{-6}	740	0	-	2.4	No	Not failed	-
217A2E	292	0.3	5×10^{-5}	772	0	0.3	3.3	No	Ductile, split	Dimple
217A2F	292	28.9	5×10^{-7}	775	0	-	1.3	No	Not failed	-
217A4C	325	25.5	5×10^{-7}	459	36.0	61.5	4.7	No	Pinhole, X-mark	Pseudocleavage
217A4E	325	44.1	2×10^{-7}	845	189.7	233.8	6.0	No	Pinhole, X-mark	Pseudocleavage
217A4F	325	51.5	1×10^{-7}	740	40.0	91.5	4.7	No	Pinhole, X-mark	Pseudocleavage
217B2D	325	51.9	7×10^{-8}	1016	185.9	237.8	6.0	No	Ductile, split	Dimple
217A4G	325	87.4	3×10^{-8}	460	247.8	335.2	3.6	Yes	Pinhole, X-mark	Pseudocleavage
217B2C	325	18.3	2×10^{-8}	500	673.5	691.8	4.7	Yes	Pinhole, X-mark	Pseudocleavage

^aFuel burnup 27.7 MWd/kg U, cladding fluence ($E > 0.1$ MeV) 4.4×10^{21} n/cm²; tests conducted in a flowing-argon environment.

^bDiametral strain measured after termination of test. Failure strains not known but smaller than these values (see text).

observed, as listed in the tables. Table I indicates that the failures associated with a large extent of pseudocleavage correspond to a small diametral strain. The final strains measured for the expanding-mandrel test specimens are considerably larger, as shown in Table II. However, as pointed out previously, this originates from the difficulty of detecting the exact failure moment under the mandrel loading condition. Because of this difficulty, the loading could not be terminated in time, and, as a result, specimen deformation continued even after a throughwall failure occurred.

Crack Morphologies

Examinations of metallographic cross sections and crack distributions on the inner and outer surfaces of the failure region showed that cracks leading to failure in all of the internal gas-pressurization tests (Table I) initiated at the outer surface and propagated toward the inner surface [30]. One of the characteristics of the spent-fuel cladding is the significant thicknesses of the outer-surface oxide layers (Table I) produced as a result of the in-service corrosion. Owing to these thick oxide layers, significant intrinsic hoop (tensile) stress is produced in the metallic layer at the oxide-metal boundary as a result of volume expansion accompanying the Zircaloy-to-oxide phase transformation. The stress is comparable in magnitude to the applied hoop stress [30]. Consequently, the effective stress at the outer surface will be significantly larger than that at the inner surface, and a crack will be nucleated at the oxygen-rich metal near the oxide-metal boundary and propagate toward the inner surface. Such cracks were absent in regions where the oxide layer spalled, thus relieving the intrinsic hoop stress [30]. A further experiment showed that when the oxide layer on a portion of the outer surface was removed by mechanical abrasion and the specimen was subsequently loaded to fracture by internal gas pressurization, cracks initiated on the

inner surface and propagated toward the oxide-free outer-surface region [35]. This observation is in agreement with the explanation based on the oxide layer-induced intrinsic hoop stress. If a similar spent-fuel cladding specimen was internally pressurized with an SCC agent such as iodine, the crack propagation would be in the opposite direction, which is the case reported in Ref. 32.

In contrast to the crack propagation behavior under gas-pressurization loading, the expanding-mandrel tests resulted in cracks which nucleated on the inner surface and propagated toward the outer surface. This is shown in Fig. 2. A typical throughwall crack is shown at the cross point of "X-marks" in Fig. 2(A). An examination of the distribution of the numerous cracks located on the inner surface shows, however, that the cracks nucleated at the inner surface adjacent to the expanding ring [Figs. 2(B) and (C)]. The direction of the crack propagation can also be confirmed from metallographic cross sections [Fig. 2(D)], which show a throughwall crack and numerous incipient cracks at the inner diameter but no such cracks at the outer diameter. Under the expanding-mandrel loading, the stress at the inner surface has been calculated to be 3-4 times larger than that at the outer surface, and in such a situation, the crack will propagate from the inner to the outer surface even for the oxide-layer-covered spent-fuel cladding [36].

The "X-marks" and the crack morphologies shown in Fig. 2 are similar to those observed in PCI-defected fuel rods. Similar morphologies and "X-marks" for other specimens listed in Table II have been reported elsewhere [37].

SEM Fractographs

Typical fracture surface morphologies of Zircaloy-2 specimens that failed in a ductile and a brittle manner under internal gas-pressurization loading are shown in Figs. 3(A) and (B), respectively. The brittle-type fracture

Fig. 2. Morphologies of brittle cracks produced in expanding-mandrel tests on H. B. Robinson cladding at 325°C. (A) Overall view of specimen tube showing a throughwall crack at the cross point of an "X-mark"; (B) inner-surface crack morphologies near the expanding-ring mark; (C) higher magnification of the outlined area of (B); (D) circumferential cross section showing a branching throughwall crack and numerous incipient cracks at the inner surface.

Fig. 2. (Contd.)

Fig. 3. Typical SEM fracture surface morphologies obtained in internal gas-pressurization tests on Zircaloy-2 cladding. (A) Ductile failure; (B) and (C) pseudocleavage from brittle failure.

surface morphology shown in Fig. 3(B), that is, a typical "pseudocleavage plus fluting" fracture, is similar to what has been reported by Rosenbaum et al. [38] for incipient defects in a Zircaloy-2 spent-fuel cladding from the Dresden-III boiling-water reactor. In the Zircaloy-4 spent-fuel cladding from the H. B. Robinson reactor, fracture surface morphologies similar to those in Figs. 3(B) and (C) have been observed in the gas-pressurization tests (Table I).

Fracture surface morphologies of the H. B. Robinson cladding specimens subjected to expanding-mandrel tests (Table II) are shown in Figs. 4 and 5. As in the case of the internal gas-pressurization tests, morphologies similar to those of Figs. 3(B) and (C) were found. The fracture surface morphology shown in Figs. 5(B) and (C) appears somewhat different. Nevertheless, the morphology indicates propagation of a brittle-type crack in the specimen. Narrow strips of ductile "dimple" features were frequently observed near the outer surfaces of several brittle-failure specimens, indicating a brittle-to-ductile transition of the crack propagation. The characteristic morphologies shown in Figs. 4 and 5 are similar to the limited number of fractographs reported in the literature for PCI-defected fuel claddings from pressurized-water and test reactors [17,39-41].

Fracture surfaces of specimens that underwent ductile failure in expanding-mandrel tests (Table II) showed only dimple features similar to Fig. 3(A). Ductile-failure specimens were also characterized by a fracture tip that showed some wall thinning and an $\sim 45^\circ$ shear in the circumferential cross section. Normal hydride stringers oriented in both the circumferential and radial directions were observed in the metallographic cross sections. However, no correlation was noted between the orientation of the optically observed δ -hydride stringers and the fractographic characteristics.

Fig. 4. Fracture surface morphology of H. B. Robinson cladding tube 217A4G subjected to expanding-mandrel test at 325°C. (A) Overall view of the fracture surface; (B), (C), and (D) higher magnifications of circled areas I, II, and III of (A), respectively, showing pseudocleavage.

Fig. 4. (Contd.)

Fig. 4. (Contd.)

Fig. 4. (Contd.)

Fig. 5. Fracture surface morphology similar to that of Fig. 4 but from cladding tube 217A4C. (A) Overall view; (B) and (C) higher magnifications of circles 1 and 2 near the inner surface of (A), respectively, showing pseudocleavage.

TEM Microstructures

Zr₃O Precipitates

TEM-HVEM examination of thin-foil specimens obtained from regions adjacent to ductile-failure sites showed a high density of dislocations and dislocation entanglements. The dislocations in the ductile-failure specimens were typically observed with the $\{10\bar{1}0\}$ or $\{10\bar{1}1\}$ of the matrix reflections operating. Tilting and dark-field imaging experiments showed a normal Burgers vector for the dislocations, that is, $\frac{1}{3} \vec{a} \langle 11\bar{2}0 \rangle$.

In contrast to this, the specimens that failed in a brittle manner with a characteristically large extent of pseudocleavage on the fracture surface showed comparatively few dislocations and dislocation substructures. Practically all the dislocations in the brittle-type specimens were observed with the $\{0002\}$ of the matrix in strong reflection. When examined in a bright field, images corresponding to radiation-induced defects and small dark precipitates (≤ 10 nm) were usually clustered around the dislocation substructures. Careful examination of the corresponding selected-area diffraction (SAD) patterns of regions containing the dislocation substructures frequently showed superlattice reflections of the Zr₃O phase, which has been reported for irradiated specimens in Ref. 30. A typical example of the characteristic dislocation substructure and SAD pattern is shown in Fig. 6. The SAD pattern of Fig. 6(B) was obtained from the center of the bright-field image of the dislocation substructure of Fig. 6(A). In the pattern, rows of Zr₃O superlattice reflections as well as α -Zr reflections are observed parallel to the row of strong reflections of $\{0002\}_{\alpha}$. The superlattice reflections are characteristically diffuse and very weak, in contrast to the sharp, strong reflections of the α -Zr. Because of the extremely low intensity, the superlattice spots could not be detected on the microscope screen. They could

Fig. 6. TEM micrographs obtained from regions adjacent to the brittle-fracture site of Big Rock Point cladding tube 165AE4B fractured under internal gas pressurization at 325°C. (A) Bright-field morphology of a dislocation substructure; (B) indexed SAD pattern showing Zr_3O superlattice reflections; (C) dark-field image obtained from the (0002) reflections. Subscripts α , s, χ , and C in the SAD pattern denote, respectively, α -Zr, Zr_3O , surface χ -hydride, and cubic- ZrO_2 phases.

be identified only through a careful examination of the original negatives of the SAD patterns on a light table. In the characteristic SAD pattern exemplified by Fig. 6(B), identification of the superlattice spots is facilitated since the rows of these spots not only lie parallel to the $\{0002\}_\alpha$ row, but also form a rectangular cross grid with the $\{0002\}_\alpha$ row. There are a total of 18 superlattice- and 10 fundamental-reflection rows in which the d-spacing of the closest spot is larger than 0.056 nm [34]. Among the 10 fundamental-reflection rows, only two rows, that is, the rows containing $(30\bar{3}0)_{\text{Zr}_3\text{O}}$ and $(63\bar{9}0)_{\text{Zr}_3\text{O}}$, will show corresponding lower-order superlattice reflections if the zone axis is properly oriented. Therefore, in practice, the chance of obtaining a SAD pattern that contains both the superlattice- and fundamental-reflection rows is very slim. The primary difficulty was that the specimen could not be properly tilted since the superlattice reflections were always invisible on the microscope screen. Because of this difficulty, no dark-field images could be obtained from the superlattice reflections.

The HVEM was advantageous for diffraction experiments because of its greater reflecting sphere and superior accuracy in producing diffraction patterns. In the HVEM-SAD pattern shown in Fig. 7(B), two rows of superlattice reflections containing $(31\bar{4}0)_{\text{Zr}_3\text{O}}$ and $(\bar{3}\bar{1}40)_{\text{Zr}_3\text{O}}$ are observed. The orientation revealed in the pattern, that is, $[\bar{5}410]_\alpha (12\bar{3}0)_\alpha // [57\bar{2}0]_{\text{Zr}_3\text{O}}$ $(31\bar{4}0)_{\text{Zr}_3\text{O}}$, is identical with that reported by Holmberg and Dagerhamn [42]. A careful examination of the dark-field images of dislocations seen in Figs. 6(C) and 7(C) shows that these images were produced by fine particles 2-6 nm in size which decorated the dislocations. A similar example is shown in Fig. 7(D). Such images of very fine precipitates decorating dislocations could be obtained only by weak-beam dark-field techniques [43,44], with typical exposure times of 45-90 s. Under bright-field or strong dark-field

Fig. 7. HVEM micrographs obtained from regions of H. B. Robinson cladding adjacent to the brittle-fracture site after expanding-mandrel test at 325°C. (A) Bright-field morphology of a dislocation substructure; (B) indexed SAD pattern showing cubic-ZrO₂ and Zr₃O-superlattice reflections; (C) dark-field image obtained from the (0002) reflections, showing dislocations decorated by Zr₃O particles 2-6 μm in size; (D) dark-field image similar to (C) but from another nearby dislocation substructure. The letter D denotes multiple diffraction spots.

Fig. 7. (Contd.)

imaging conditions, the fine precipitates were not revealed. This appears to be the case for similar bright-field and dark-field images previously reported in Refs. 45 and 38, respectively, which showed dislocation structures in highly irradiated Zircaloy cladding.

A large number of SAD patterns were obtained from regions containing dislocation substructures, and the patterns were analyzed for the presence of Zr_3O superlattice reflections. The results for the brittle-failure specimen 165AE4B [see Fig. 3(B) for fracture surface morphology] are listed in Table III. Out of a total of 36 SAD patterns analyzed, 22 (61.5%) contained the superlattice reflections. Similar results for the 165AE4A specimen, which failed in a ductile manner [see Fig. 3(A) for fracture surface morphology], are listed in Table IV. In contrast to the brittle-failure specimen, the ductile-failure specimen showed superlattice reflections in only 9% of the analyzed SAD patterns. This comparison clearly shows that the dislocation movement in the brittle-failure specimen was significantly impeded because of the Zr_3O precipitates, and as a result, the plastic deformation in the specimen was minimized, leading eventually to a brittle-type failure. All the bright-field images of dislocations in the brittle-failure specimens of Table III were observed with the $\{0002\}_\alpha$ in strong reflection, compared to only 5 out of 31 for the ductile-failure specimens of Table IV. This, in conjunction with the relative frequency of the appearance of the superlattice reflections, indicates that the fine precipitates which decorate the dislocations in Figs. 6(C), 7(C), and 7(D) are indeed the Zr_3O particles. This is further corroborated by the following observations.

As reported in Ref. 30, diffraction patterns were frequently observed from the brittle-failure specimens that contained fundamental but not superlattice reflections of the Zr_3O phase (e.g., Figs. 6, 7, 11, and 13 of

Table III. Summary of TEM-HVEM analysis of Zr_3O superlattice reflections observed in association with dislocation substructures in the Big Rock Point spent-fuel cladding specimen 165AE4B, which failed in a brittle manner at 325°C by internal gas pressurization^a

Identification no. of selected-area diffraction pattern	Identification no. of selected-area bright-field image ^b	Identified Zr_3O superlattice reflections ^c
34350	34348	None
34132	33131	None
8606	8605	None
34137	34136	None
34141	34140	802, 803, 804, 805
34143	34142	425, 426, 427, 428
34145	34144	324, 325, 326, 327
34583	34582	101, 100, 101, 102, 103, 104, 105, 106, 106, 105, 104, 103, 102, 101, 100, 101, 200, 201, 202, 203, 204, 205, 206, 312, 313, 310, 311, 312, 313
35275	35273	None
1500	1499	207, 206, 205, 204, 203, 202, 201, 200, 201, 202, 203, 207, 206, 205, 204, 203, 202, 201, 200, 201, 202, 203
1507	1506	755, 754, 753, 752, 751, 750, 751, 752, 755, 754, 753, 752, 751, 750, 751, 752, 753, 754
34579	34577	430, 431, 432, 320, 321, 322, 323, 404, 514, 403, 513, 012, 102, 212, 024, 114, 204, 314, 504, 505, 426, 427, 216, 106, 016, 126, 713, 712, 611, 610, 611
34296	34294	626, 627, 424, 425, 426, 427
33312	33310	None
35292	35291	None
35294	35293	None
35298	35297	None

Table III. (Contd.)

Identification no. of selected-area diffraction pattern	Identification no. of selected-area bright-field image ^b	Identified Zr ₃ O superlattice reflections ^c
35300	35299	800, 80 $\bar{1}$, 80 $\bar{2}$
34589	34586	None
27172	27174	None
8039	8038	None
8049	8047	407, 408, 409, 4010, 4011, 435, 436, 437, 438, 439, 4310, 4311, 4312, 4313, 317, 318, 319, 315, 316, 317, 318, 319
6089	6087	None
34285	34284	832, 831, 830
34590	34589	None
35290	35289	43 $\bar{2}$, 43 $\bar{1}$, 430, 431, 432
35300	35299	800, 80 $\bar{1}$, 80 $\bar{2}$
35302	35301	42 $\bar{4}$, 42 $\bar{3}$, 42 $\bar{2}$, 42 $\bar{1}$, 420, 421, 422, 423, 424, 425, 71 $\bar{4}$, 71 $\bar{3}$, 71 $\bar{2}$, 71 $\bar{1}$, 710, 51 $\bar{4}$, 51 $\bar{3}$, 51 $\bar{2}$, 51 $\bar{1}$, 510, 511, 512, 513, 514 43 $\bar{2}$, 43 $\bar{1}$, 430, 431, 432, 433, 311, 312, 313, 314, 315, 316 72 $\bar{2}$, 72 $\bar{3}$, 72 $\bar{4}$, 801, 800, 80 $\bar{1}$, 80 $\bar{2}$
35305	35304	61 $\bar{2}$, 61 $\bar{1}$, 610, 611, 612
35307	35306	01 $\bar{7}$, 01 $\bar{8}$, 01 $\bar{9}$, 01 $\bar{10}$, 01 $\bar{11}$, 019, 0110, 0111
35309	35308	71 $\bar{1}$, 710, 711
8593	8590	62 $\bar{1}$, 620, 621, 622, 623, 610, 612, 613, 421, 422, 423, 514, 515, 516, 315, 316, 317, 20 $\bar{2}$, 20 $\bar{1}$, 200, 201, 202, 203, 204, 203, 20 $\bar{2}$, 20 $\bar{1}$, 200, 201, 202, 203, 204 202, 203, 204, 202, 203
34358	34361	43 $\bar{2}$, 43 $\bar{1}$, 430, 32 $\bar{3}$, 32 $\bar{2}$, 32 $\bar{1}$,
34587	-	

^aFor information on burnup, fluence, mechanical test conditions, and SEM fractographic and metallographic characteristics, see Ref. 30.

^bBright-field image of the selected area containing the dislocation substructures.

^cDenoted in Miller indices.

TABLE IV. Summary of TEM-HVEM analysis of Zr_3O superlattice reflections observed in association with dislocation substructures in the Big Rock Point spent-fuel cladding specimen 165AE4A, which failed in a ductile manner at 325°C by internal gas pressurization^a

Identification no. of selected-area diffraction pattern	Identification no. of selected-area bright-field image ^b	Identified Zr_3O superlattice reflections ^c
35356	35355	None
35358	35357	None
35360	35359	None
35362	35361	None
35364	35363	None
35372	35371	None
35366	35365	None
35368	35367	$4\bar{4}3$, $5\bar{3}2$, $6\bar{2}1$
35374	35373	103, 104, 105, 106, 107, $2\bar{1}4$, $2\bar{1}3$, $2\bar{1}2$, $2\bar{1}1$, $2\bar{1}0$, $2\bar{1}1$, $2\bar{1}2$, $2\bar{1}3$, $2\bar{1}4$, $2\bar{1}2$, $2\bar{1}1$, $2\bar{1}0$, $2\bar{1}1$, $2\bar{1}2$
35379	35378	None
35370	35369	$3\bar{1}2$, $2\bar{0}3$, $1\bar{1}4$
26675	26674	None
26670	26669	None
26651	26652	None
34169	34168	None
26658	26659	None
34178	34176	None
26666	26667	None
34180	34179	None
34783	34782	None
26743	26744	None
00038	00037	None
00041	00040	None
00045	00044	None
00056	00055	None
00066	00065	None
00019	00018	None
00022	00020	None
00027	00026	None
26980	26981	None
26988	26995	None

^aFor information on burnup, fluence, mechanical test conditions, and SEM fractographic and metallographic characteristics, see Ref. 30.

^bBright-field image of the selected area containing the dislocation substructures.

^cDenoted in Miller indices.

Ref. 30). Such situations arise for certain zone axes of Zr_3O or when the degree of the ordering of oxygen interstitials is decreased because of an increased nonstoichiometry in the phase. The latter situation is similar to the intensity of the superlattice reflections of γ -zirconium hydride [46]. Since the Zr_3O fundamental reflections were intense enough to be identified on the microscope screen, their corresponding dark-field images could be obtained. An example of such dark-field images, Fig. 8(C), shows nearly spherical precipitates 2-6 nm in size. The size and morphology of the precipitates that decorate the dislocations in Figs. 6(C), 7(C), and 7(D) are similar to those of Fig. 8(C), which is the image obtained from the $(\bar{1}2\bar{1}1)_{Zr_3O}$ reflection. This similarity indicates that the former precipitates are indeed the Zr_3O phase. The (0002) reflection of α -Zr ($d = 0.257$ nm) can be virtually superimposed on (002) reflections of the following phases: Zr_3O ($d = 0.2598$ nm); the χ -hydride ($d = 0.257$ nm), which is an artifact surface hydride [30]; cubic Zr_3O ($d = 0.2567$ nm); and monoclinic ZrO_2 ($d = 0.2539 - 0.262$ nm), which is also a surface phase [47]. Reflections of the χ -hydride, cubic ZrO_2 , and monoclinic ZrO_2 away from the (002) row could be identified and their dark-field images were examined. However, none of them showed images of precipitates that decorated the dislocations. This leaves only the Zr_3O reflections, and thus corroborates the conclusion that the characteristic dislocations observed in the brittle-failure specimens were decorated by Zr_3O precipitates.

A further interesting point is that if the characteristic dislocations were indeed $\vec{c}$ -component dislocations, as claimed in Refs. 38 and 45, one would expect images of continuous black-white strain contrast, possibly with frequent gaps similar to what has been observed by Allen and Van der Sande in

TEM, the angle of the electron path changes slightly. Therefore, the two images can be used effectively as a "pseudo-stereopair." By viewing the resulting micrographs with a stereoscope, one can readily distinguish between a bulk and a surface phase. Examples of such dark-field stereopairs are shown in Fig. 9. HVEM was found to be advantageous for showing the bulk distribution, since a thicker region can be examined. The indexed SAD pattern of Fig. 9(B) shows the presence of cubic-ZrO₂ phase in the recrystallized grain at the center of Fig. 9(A). Dark-field stereopairs produced from the (111) and (11 $\bar{1}$) reflections of the cubic ZrO₂ are shown, respectively, in Figs. 9(C, D) to 9(E). The stereopairs clearly show a distribution of bulk precipitates of cubic ZrO₂ ~10 nm in size. In many cases, the cubic ZrO₂ reflections and the primary reflections of the surface χ -hydride are located at virtually identical spots [47]. However, stereoviews similar to Figs. 9(C)-(E) show the bulk nature of the cubic-ZrO₂ particles and the surficial nature of the χ -hydride phase. Similar stereopairs showing the surficial nature of the monoclinic-ZrO₂ phase have also been reported [47]. Identification of the surface precipitates, which can be located on either the top or bottom surface of the thin foil, is facilitated by switching the positions of the two matching micrographs. The switch reverses the surfaces coming into view, and hence, facilitates identification of bulk precipitates.

The cubic-ZrO₂ precipitates were also observed in aggregation in the form of curved threads, as shown in Fig. 10(C). As demonstrated by the comparisons of the bright- and dark-field images in Figs. 9 and 10, detection of the cubic-ZrO₂ precipitates from a bright-field image was difficult. Since the precipitate reflections are also usually very weak and diffuse [e.g., Fig. 10(B)] in the diffraction mode, careful effort was required to identify

Fig. 9. HVEM micrographs obtained from brittle-fracture site of H. B. Robinson cladding tube 217A4G after expanding-mandrel test at 325°C. (A) Bright-field image showing a recrystallized grain; (B) indexed SAD pattern obtained from the center of the grain, showing (110) zone of cubic ZrO₂; (C) weak-beam dark-field stereopair obtained from the (111) reflections of the bulk cubic-ZrO₂ and artifact surface χ -hydride phases; (D) stereopair of higher magnification of (C); (E) dark-field stereopair obtained from the (111) reflections of the cubic-ZrO₂ phase. Note ~1.7° difference between (110)_α and (002)_c in (B).

Fig. 9. (Contd.)

Fig. 10. TEM micrographs obtained from brittle-fracture site of H. B. Robinson cladding tube 217A4G after expanding-mandrel test at 325°C. (A) Bright-field image of a recrystallized grain; (B) indexed SAD pattern showing reflections from cubic ZrO_2 , bulk zirconium hydride, and artifact surface χ -hydride; (C) weak-beam dark-field stereopair obtained from the $(2\bar{2}0)$ reflections of cubic ZrO_2 and χ -hydride and $(\bar{1}\bar{1}20)$ reflection of α -Zr, showing bulk cubic ZrO_2 with both particle- and thread-like morphologies. Letters γ in (A) and (B) and C in (C) denote, respectively, bulk hydride and cubic- ZrO_2 precipitates.

Fig. 10. (Contd.)

Fig. 10. (Contd.)

the reflections and to obtain dark-field images. The weak-beam dark-field images that were obtained usually revealed surprisingly large densities of the fine precipitates [e.g., Figs. 9(C)-(E)]. In the thin-foil regions that characteristically contained a high density of the precipitates, virtually no dislocations were observed. This indicates a general embrittlement of the material, at least in the selected local region, and appears to be associated with the brittle-type fracture.

Bulk Zirconium Hydride

In thin-foil regions which originated from a brittle-fracture site and which contained copious precipitates of cubic ZrO_2 , another type of precipitate was frequently observed. Such precipitates are denoted by the " γ " arrows in Fig. 10(A). The precipitate size is typically 35-100 nm, an order of magnitude larger than the Zr_3O or cubic- ZrO_2 particles but still too small to be visible in an optical or scanning electron microscope. Although not conclusive, the precipitates appear to be δ (rather than γ) zirconium hydride from analyses of SAD patterns of several different zone axes. Examination of stereopairs of dark-field images [e.g., Fig. 11] showed that the hydrides were also a bulk phase. The dark-field stereopair shown in Fig. 11(A) was produced from an aperture containing ($\bar{2}\bar{2}\bar{2}$) reflections of the cubic ZrO_2 (d-spacing 0.1482 nm), bulk hydride (0.136-0.138 nm), and surface χ -hydride (0.150 nm) [47]. Visible in the stereopair are bulk cubic- ZrO_2 precipitates in the form of either short strings or particles ~ 10 nm in size, bulk hydrides 50-100 nm in size, and artifact surface χ -hydrides ~ 10 nm in size. Dark-field images of the bulk hydrides, produced as a result of leakage of the central bright-field beam, are also visible in Fig. 11(A). A similar dark-field stereopair in Fig. 11(B) shows images obtained from ($1\bar{1}\bar{1}$) reflections of the bulk hydride and cubic ZrO_2 , and from the (111) reflection of monoclinic ZrO_2 . The

Fig. 11. Dark-field stereopairs similar to Fig. 10(C) but obtained from the following: (A) $(\bar{2}2\bar{2})$ reflections of the cubic ZrO_2 , bulk hydride, and surface χ -hydride; (B) $(\bar{1}11)$ reflections of the cubic ZrO_2 (small particles ~ 10 nm in size) and bulk hydride (large precipitates ~ 30 nm in size), and (111) reflections of the surface monoclinic ZrO_2 (diffuse film).

Fig. 11. (Contd.)

surficial nature of the diffuse film of the monoclinic oxide can be clearly discerned from the stereoview of Fig. 11(B).

The bulk hydride shown in Figs. 10 and 11 is different from the δ -hydrides that are commonly observed metallographically in spent-fuel cladding. The δ -hydride is shaped like a long bar, with a length of the order of ~ 1000 nm. As a result, it is readily observed in optical micrographs. The smaller bulk hydrides were always observed in association with a copious precipitation of the cubic- ZrO_2 particles. Characteristic microstructures containing both the cubic ZrO_2 and the small bulk hydride (e.g., Figs. 10 and 11) were observed only for brittle-failure specimens but not for ductile or unirradiated specimens.

Chemical analysis of the TEM thin foils of the brittle specimen described in Figs. 10 and 11 showed oxygen and hydrogen contents of 2326 and 67 wt. ppm, respectively. The unusually high level of oxygen in the metal is consistent with the TEM observation of the oxide precipitates.

DISCUSSION

The association of the Zr_3O and cubic- ZrO_2 precipitates with dislocations in the brittle-failure specimens shows that the dislocation motion in the specimens during the loading at 325°C was impeded by the precipitates. The immobilization of dislocations should be conducive to a brittle-type fracture, since no other deformation mode (such as twinning) was observed to any appreciable extent. Interactions between oxygen and dislocations, similar to those observed during strain aging of unirradiated Zircaloy, may have occurred during the loading at 325°C . However, the distinct particle-like morphologies of the dark-field images of the Zr_3O and cubic- ZrO_2 phases (Figs. 7-11) indicate irradiation-induced precipitation of the phases during the in-reactor

service. This observation, and its implication that oxygen interacts with the radiation-induced defects, are consistent with a prediction [30] based on the theory of radiation-induced segregation as well as with the observation of the radiation-anneal hardening phenomenon in Zircaloy [21-23]. Although their relative importance is not known, it is believed that the radiation-induced precipitation and the strain aging played a primary role in the evolution of the brittle-type fractures reported in this study.

To demonstrate precipitation of the Zr_3O and cubic ZrO_2 phases during in-situ irradiation at the test temperature, some TEM thin-foil specimens from the brittle-fracture tubes were irradiated by 1-MeV electrons in the HVEM in a vacuum of $\sim 1.3 \times 10^{-4}$ Pa at 325°C [31]. During the in-situ irradiation, bright-field images of precipitates or defects were visible in increasing number. In the corresponding SAD patterns, strong reflections of cubic ZrO_2 and weak Zr_3O superlattice reflections that were not present before the 325°C irradiation were observed. Dark-field imaging confirmed a precipitation of cubic- ZrO_2 particles which were somewhat smaller than those observed in the as-irradiated and as-tested specimens. The in-situ irradiation experiment clearly showed that radiation-induced precipitation of Zr_3O and cubic ZrO_2 is possible at 325°C. Similar precipitation of $Ti_3(O_{1-x}N_x)$ on dislocation substructures has been reported by Loomis and Zaluzec [54] after irradiation by 4-MeV Ni ions of a V-15Cr-5Ti alloy containing nonmetallic impurities. Our in-situ irradiation of the brittle specimen described in Fig. 11 also showed that the small bulk hydrides did not dissolve at 325°C; hence, they could contribute to embrittlement of the specimen during the expanding-mandrel test at high temperature. In contrast, dissolution of the surface χ -hydrides was frequently observed when they were heated by concentrated electron beams.

A prediction of the range of radiation-induced segregation in a simple temperature/dose-rate diagram has been reported by Okamoto and Rehn [55]. According to the diagram, which is illustrated in Fig. 12, recombination of radiation-induced vacancies and interstitials is predominant if the temperature is below a certain threshold which depends on dose rate. At higher temperatures, the recombination is negligible since the radiation-induced defects are sufficiently mobile and tend to anneal out at sinks such as surfaces, voids, and grain boundaries. However, for an intermediate temperature range, radiation-induced segregation, and hence, precipitation can be expected to occur. According to the sample calculation reported by Orlander [56], a fast (>0.2 MeV) neutron flux of $\sim 5 \times 10^{13}$ n/cm² s⁻¹, which is expected for light-water reactor operating conditions, corresponds to an approximate dose rate of 5×10^{-8} displacements per atom (dpa) per second. As shown in Fig. 12, a cladding temperature between 300 and 340°C (i.e., $T/T_m = 0.27-0.29$, where T_m is the alloy melting temperature in K), which is the temperature expected for normal operating conditions, corresponds roughly to an optimum condition for radiation-induced segregation for this dose rate. Unfortunately, this fact, as well as the strain-aging maximum observed for a similar temperature range [18], appears to indicate that the susceptibility of water-reactor Zircaloy fuel rods to low-ductility brittle-type failures would be most pronounced at 300-340°C, which encompasses the range of reactor operating temperatures. It also implies a significantly reduced susceptibility at a lower temperature, e.g., 250°C, under otherwise identical conditions. For fully recrystallized cladding material in which the predominant sink for the defect-oxygen complex would be grain boundaries rather than dislocations, precipitation of the Zr₃O or cubic ZrO₂ would be expected

Fig. 12. Expected occurrence of irradiation-induced segregation as a function of temperature (divided by melting temperature of the alloy) and dose rate (in displacements per atom per second), from Ref. 55. Zircaloy cladding under water reactor operating conditions corresponds roughly to an optimum condition for radiation-induced segregation.

primarily at the grain boundaries. In an extreme case this could lead to an intergranular failure. Some grain boundary precipitation of the Zr_3O phase is, in fact, visible in the dark-field micrograph of Fig. 8(C).

Embrittlement by the synergistic effects, which involve oxygen, irradiation, and strain aging, augmented by the precipitation of the small bulk hydrides, indicate that a suppression of oxygen content and corrosion at the inner surface of cladding would be critical in reducing the susceptibility to brittle crack formation. The low-ductility brittle-type failures reported in Refs. 14-17 for very fast ramping conditions can also be explained on the basis of the synergistic embrittling mechanism. This could be confirmed through microstructural examinations similar to those reported here. In any event, the present results may stimulate a reevaluation of the bases of the PCI-failure mechanism (or mechanisms) reported in the literature, with particular reference to the behavior of power-reactor fuel claddings. Of particular importance in elucidating the mechanism(s) would be microstructural evaluations of PCI-defected commercial cladding specimens as well as PCI-resistant (e.g., graphite-coated or Zr-lined) claddings. It appears that evidence based on macroscopic characteristics, such as the salient features of fractographs, should be deemed only as corroborative in nature.

CONCLUSIONS

1. PCI-like brittle-type failures, characterized by "X-marks" on the outer surface, pseudocleavage in the fracture surface, and brittle cracks on the inner surface and in the cross section, have been produced at 325°C by expanding-mandrel tests on power-reactor spent-fuel cladding tubes in inert gas environments. The occurrence of the brittle-type failures is

consistent with the results of similar tests by internal gas pressurization. A major difference between the results of the two tests is the direction of crack propagation; under the expanding-mandrel loading the crack nucleated on the inner surface of the cladding and propagated toward the outer surface while under the gas pressurization loading the opposite occurred. The difference is consistent with the stress distribution across the tube wall in which a significant intrinsic hoop stress is present owing to the outer-surface oxide layer.

2. Ductile-failure specimens were characterized by a comparatively high density of dislocations which showed normal $\vec{a}$ -type Burgers vector.
3. Brittle-failure specimens were characterized by comparatively few dislocations which formed substructures. The dislocations were decorated by Zr_3O precipitates 2-6 nm in size, and cubic- ZrO_2 precipitates $\lesssim 10$ nm in size were also observed in association with most of the dislocation substructures; these observations indicated a general immobilization of the dislocations. The low-ductility brittle-type failures appear to have been produced primarily as a result of the dislocation immobilization by the Zr_3O and cubic- ZrO_2 precipitates, augmented by precipitates of bulk hydrides 35-100 nm in size. The bulk nature of the precipitates was demonstrated by " ^{210}D -microscopy" of weak-beam dark-field images.
4. The Zr_3O and cubic- ZrO_2 particles observed in the spent-fuel cladding specimens formed during in-reactor service primarily via radiation-induced precipitation. Formation of the precipitates was also observed during 1-MeV electron irradiation at 325°C in the HVEM.

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REFERENCES

- [1] Rosenbaum, H. S., *Electrochemical Technology*, Vol. 4, 1966, p. 153.
- [2] Grubb, W. T. and Morgan, M. H., III, in Zirconium in the Nuclear Industry (Fourth Conf.), ASTM STP 681, American Society for Testing and Materials, 1979, pp. 145-154.
- [3] Sejnoha, R. and Wood, J. C., *ibid.*, pp. 261-184.
- [4] Orlander, D. R., *Journal of Nuclear Materials*, Vol. 110, 1982, pp. 343-345.
- [5] Shann, S. H. and Orlander, D. R., *Journal of Nuclear Materials*, Vol. 113, 1983, pp. 234-248.
- [6] Une, K., *Journal of Nuclear Materials*, Vol. 87, 1979, pp. 207-210.
- [7] Östberg, G., *Journal of the Institute of Metals*, Vol. 93, 1964-65, pp. 223-228.
- [8] Sabol, G. P. and McDonald, S. G., *Journal of Nuclear Materials*, Vol. 64, 1977, p. 223.
- [9] Leech, N. A. and Garlick, A., *Journal of Nuclear Materials*, Vol. 125, 1984, pp. 19-24.
- [10] Holub, F., *Journal of Nuclear Materials*, Vol. 130, 1985, pp. 534-541.

- [11] Ross-Ross, P. A., Dunn, J. T., Mitchell, A. B., Towgood, G. R., and Hunter, T. A., AECL-5261, Atomic Energy of Canada Ltd. (January 1976). See also Proc. European Nuclear Conf. on Nuclear Energy Maturity, 1975, Paris, France, Vol. 3, p. 85.
- [12] Videm, K. and Lunde, L., in Proc. ANS Topical Meeting on Water Reactor Fuel Performance, May 9-11, 1977, St. Charles, IL, pp. 274-281.
- [13] Cox, B. and Aldridge, S. A., Journal of Nuclear Materials, Vol. 67, 1977, pp. 55-66.
- [14] Lowry, L. M., Markworth, A. J., Perrin, J. S., and Landow, M. P., Evaluating Strength and Ductility of Irradiated Zircaloy Task 5, Quarterly Progress Report, July-September 1979, NUREG/CR-1571, Battelle Columbus Laboratories.
- [15] Lowry, L. M., Perrin, J. S., Markworth, A. J., and Gallagher, W. J., Evaluating Strength and Ductility of Irradiated Zircaloy Task 5, Semiannual Progress Report, July-December 1978, NUREG/CR-0981, BMI-2020.
- [16] Bergenlid, U., Lysell, G., Mogard, H., and Rönnerberg, G., in Proc. Specialists' Meeting on Pellet Cladding Interaction in Water Reactor Fuel, October 3-5, 1983, Seattle, IWGFPT/18, International Atomic Energy Agency, pp. 50-55.
- [17] Bain, A. S., Wood, J. C., and Coleman, C. E., in Proc. Intl. Conf. on Nuclear Fuel Performance, October 15-19, 1973, Westminster, London, pp. 56.1-56.5.
- [18] Kelly, P. M. and Smith, P. D., Journal of Nuclear Materials, Vol. 46, 1973, p. 23.
- [19] Thorpe, W. R. and Smith, I. O., Journal of Nuclear Materials, Vol. 78, 1978, p. 49.

- [20] Thorpe, W. R. and Smith, I. O., Journal of Nuclear Materials, Vol. 80, 1979, p. 35.
- [21] Snowden, K. U. and Veevers, K., Radiation Effects, Vol. 20, 1973, pp. 169-174.
- [22] Onchi, T., Kayano, H., and Higashiguchi, Y., Journal of Nuclear Materials, Vol. 88, 1980, pp. 226-235.
- [23] Onchi, T., Kayano, H., and Higashiguchi, Y., Journal of Nuclear Materials, Vol. 116, 1983, pp. 211-218.
- [24] Veevers, K. and Rotsey, W. B., Journal of Nuclear Materials, Vol. 27, 1968, p. 108.
- [25] Lee, D. and Koch, E. F., Journal of Nuclear Materials, Vol. 50, 1974, p. 162.
- [26] Jostsons, A., Kelly, P. M., Blake, R. G., and Farrell, K., in Effects of Radiation on Structural Materials, ASTM STP 683, J. A. Sprague and D. Kramer, eds., American Society for Testing and Materials, 1979, pp. 46-61.
- [27] Zee, R. H., Rogerson, A., Carpenter, G. J. C., and Watters, J., Journal of Nuclear Materials, Vol. 120, 1984, p. 223.
- [28] Nolfi, F. V., ed., Phase Transformation During Irradiation, Elsevier Science Publishing Co., 1983.
- [29] Chung, H. M., Transactions of the American Nuclear Society, Vol. 45, 1983, pp. 285-287.
- [30] Chung, H. M., in Proc. Intl. Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, August 22-25, 1983, Myrtle Beach, SC, pp. 297-333.

- [31] Chung, H. M., to be presented at Second Intl. Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, September 9-12, 1985, Monterey, CA.
- [32] Yaggee, F. L., Mattas, R. F., and Neimark, L. A., Characterization of Irradiated Zircalloys, EPRI NP-1155, Argonne National Laboratory, September 1979, pp. 8-1 to 8-12.
- [33] Materials Science and Technology Division Light-Water-Reactor Safety Research Program: Quarterly Progress Report, April-June 1982, NUREG/CR-2970 Vol. II, Argonne National Laboratory, pp. 72-100.
- [34] Ibid., July-September 1983, NUREG/CR-3689 Vol. III, pp. 24-28.
- [35] Ibid., January-March 1983, NUREG/CR-3689 Vol. I, pp. 113-121.
- [36] Ibid., July-September 1981, NUREG/CR-2437 Vol. III, pp. 70-92.
- [37] Ibid., April-June 1983, NUREG/CR-3689 Vol. II, pp. 98-114.
- [38] Rosenbaum, H. S., Wolff, U. E., and Bell, W. L., in Determination and Microscopic Study of Incipient Defects in Irradiated Power Reactor Fuel Rods, EPRI NP-812, Electric Power Research Institute, July 1978, pp. 3-93 to 3-166.
- [39] Aas, S. Olshausen, K. D., and Videm, K., in Proc. Intl. Conf. on Nuclear Fuel Performance, October 15-19, 1973, London, England, pp. 55.1 to 55.6 and s4.1 to s4.5.
- [40] Fuhrman, N., Pasupathi, V., and Corsett, L. V., in Proc. American Nuclear Society Topical Meeting on Water Reactor Fuel Performance, May 9-11, 1977, St. Charles, IL, pp. 262-272.
- [41] Roberts, J. T. A., Jones, R. L., Cubicciotti, D., Miller, A. K., Wachob, H. F., Smith, E., and Yaggee, F. L., Zirconium in the Nuclear Industry (Fourth Conf.), ASTM STP 681, American Society for Testing and Materials, 1979, pp. 285-300.

- [42] Holmberg, B. and Dagerhamn, T., Acta Chemistry Scandinavia, Vol. 15, 1961, p. 919.
- [43] Cockayne, D. J. H., in Diffraction and Imaging Techniques in Material Science, S. Amelinckx, R. Gevers, and J. Van Landuyt, eds., North Holland, 1978, Vol. I, pp. 153-183.
- [44] Allen, R. M. and Van der Sande, J. B., in Electron Microscopy and Analysis, 1979, Proc. Institute of Physics Electron Microscopy and Analysis Group Conf. (EMAG79), September 3-6, 1979, Brighton, England, pp. 171-174.
- [45] Holt, R. A. and Gilbert, R. W., Journal of Nuclear Materials, Vol. 116, 1983, pp. 127-130.
- [46] Sidhu, S. S., Heaton, L. R., Campos, F. P., and Zauberis, D. D., Advances in Chemistry Series, Vol. 39, 1963, p. 87.
- [47] Light-Water-Reactor Safety Fuel Systems Research Programs: Quarterly Progress Report, July-September 1984, NUREG/CR-3980 Vol. III, Argonne National Laboratory, April 1985.
- [48] Wittels, M. C. and Sherrill, F. A., Journal of Applied Physics, Vol. 27, 1956, pp. 643-644.
- [49] Wittels, M. C. and Sherrill, F. A., Physical Review Letters, Vol. 3, 1959, pp. 176-177.
- [50] Vance, E. R. and Boland, J. N., Radiation Effects, Vol. 26, 1975, pp. 135-139.
- [51] Vance, E. R. and Boland, J. N., Radiation Effects, Vol. 37, 1978, pp. 237-239.
- [52] Parsons, J. R., Hoelke, C. W., and Gilbert, R. W., Journal of Nuclear Materials, Vol. 96, 1981, pp. 169-177.
- [53] Bell, W. L., Journal of Applied Physics, Vol. 47, 1976, pp. 1676.

- [54] Loomis, B. A. and Zaluzec, N. J., to be published in Proc. First Intl. Conf. on Fusion Reactor Materials, December 3-6, 1984, Tokyo, Japan.
- [55] Okamoto, P. R. and Rehn, L. E., Journal of Nuclear Materials, Vol. 83, 1979, p. 2.
- [56] Orlander, D. R., Fundamental Aspects of Nuclear Reactor Fuel Elements, Energy Research and Development Administration, 1976, pp. 115-116 and 400-402.