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PHASE TRANSFORMATIONS IN NEUTRON-IRRADIATED ZIRCALOYS*

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ABSTRACT

Microstructural evolution in Zircaloy-2 and -4 spent-fuel cladding specimens after ~ 3 years of irradiation in commercial power reactors has been investigated by TEM and HVEM. Two kinds of precipitates induced by the fast-neutron irradiation in the reactors have been identified, i.e., Zr_3O and cubic- ZrO_2 particles approximately 2-10 nm in size. By means of a weak-beam dark-field " $2\frac{1}{2}\text{D}$ -microscopy" technique, the bulk nature of the precipitates and the surficial nature of artifact oxide and hydride phases could be discerned. The $\text{Zr}(\text{Fe}_x, \text{Cr}_{1-x})_2$ and $\text{Zr}_2(\text{Fe}_x, \text{Ni}_{1-x})$ intermetallic precipitates normally present in the as-fabricated material virtually dissolved in the spent-fuel cladding specimens after a fast-neutron fluence of $\sim 4 \times 10^{21} \text{ ncm}^{-2}$ in the power reactors. The observed radiation-induced phase transformations are compared with predictions based on the currently available understanding of the alloy characteristics.

INTRODUCTION

It has been well established in the literature that the mechanical and corrosion properties of Zircaloy cladding used in water-reactor fuel rods are profoundly altered by neutron irradiation during the in-reactor service.¹ Despite the well-established effects of irradiation on mechanical and corrosion properties, the microstructural evolution of the Zircaloy cladding that takes place during the in-reactor irradiation and the concomitant

relationship between the microstructure and properties are not well understood. During the in-reactor irradiation, in addition to radiation-induced defects, the fuel cladding is subject to stress and compositional changes that are associated with in-service corrosion. Under such circumstances, impurity or alloying elements and the radiation-induced defects or defect sinks in the material may have synergistic effects which may lead to radiation-induced segregation and precipitation. It is also possible that some precipitates normally stable without irradiation are no longer stable under irradiation and may undergo dissolution into the matrix.

Several investigators have reported evidence of interactions between impurity or alloying elements with radiation-induced defects, which lead to a phase transformation in some cases, as well as evidence of instability of intermetallic precipitates under irradiation. Dissolution of the intermetallic precipitates $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ and $\text{Zr}_2(\text{Fe}_x\text{Ni}_{1-x})$, normally present in as-fabricated Zircalloys, has been reported for specimens irradiated by neutrons in reactor.^{2,3} Interaction or trapping of niobium with radiation-induced damage zones⁴ and TEM observation of radiation-enhanced precipitation of niobium⁵ have been reported for Zr-2.5 wt % Nb. Trapping of Sn with radiation-induced defects has been also inferred by Zee et al.⁶ from an analysis of irradiation growth behavior of Zr-Sn alloys. Similar indirect evidence of interaction of oxygen with radiation-induced defects has been reported for Zircaloy-2 by several investigators from strain aging⁷ and radiation-anneal hardening⁸⁻¹⁰ characteristics in a temperature range of 300 to 350°C.

Interaction of nonmetallic impurity or alloying elements with radiation-induced defects has been also implied from TEM microstructural investigations of irradiated Zr alloys and Zircaloy-2. From an analysis of the

characteristics of vacancy and interstitial loops in several neutron-irradiated Zr alloys, Jostsons et al.¹¹ concluded that an association of nonmetallic elements, in particular oxygen, with vacancies is very likely. Lee and Koch¹² examined the diffraction characteristics of the aligned defect structures in Zircaloy-2 irradiated with Ni ions and suggested that the aligned structure may consist of precipitates of solute atoms or a second phase. However, no conclusive evidence was given. Small precipitates $\lesssim 10$ nm in size were observed¹³ in a recent TEM-HVEM microstructural investigation of Zircaloy-2 and -4 spent-fuel cladding irradiated in commercial power reactors. The precipitates had the same structure and lattice parameters as the α -Zr matrix and frequently gave rise to double diffraction. Since radiation-induced defects would not produce double diffraction, the precipitates were deduced to be Zr_3O ; a structure identical to that of an α -Zr matrix except for oxygen ordering in the unit cell. Superlattice reflections associated with the oxygen ordering were also reported.¹³

It appears, however, that detection of bulk precipitates of $\lesssim 10$ nm in size in irradiated Zr alloys has been greatly complicated by the presence of artifact surface hydride and oxide particles^{14,15} which are formed during thin-foil preparation or in the microscope. Because of the ever-present artifact surface phases, nonmatrix reflections that are frequently detected in diffraction patterns appear to have been categorically assumed by most investigators to be "spurious" reflections originating from the artifact phases. Apparently, the validity of this assumption for irradiated Zr alloys has not been critically examined. However, in view of the above-mentioned background, it was considered necessary to reexamine the origin of the nonmatrix reflections with a specific purpose of determining whether a radiation-induced phase transformation is involved in the evolution of the

microstructure during an in-reactor irradiation. Thus, Zircaloy fuel cladding specimens irradiated in power reactors for three to four years have been chosen for our TEM microstructural investigation. Evidence for radiation-induced precipitation of bulk zirconium oxide has been obtained from the microstructural investigation, and this paper documents the observation.

EXPERIMENTAL PROCEDURES

Materials

Specimens for TEM-HVEM examination were obtained from Zircaloy-2 and -4 spent-fuel cladding sections irradiated in two operating commercial reactors, i.e., the Big Rock Point (boiling water) and H. B. Robinson (pressurized water) reactors, respectively. The fuel burnup and neutron fluence were in the range of 22 to 28 MWd/kgU and 3.3 to 4.4×10^{21} n/cm² (E > 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. Some TEM specimens were excised from the cladding sections which were subsequently fracture tested at 325°C either by internal gas pressurization or expanding mandrel techniques in an inert-gas environment. Pieces of cladding sections that contained the fracture surface were mechanically ground and TEM disks were punched from sites adjacent to the fracture surface. The as-fabricated archive materials of the spent-fuel cladding exhibited the typical crystallographic texture of commercial fuel cladding, with the basal poles oriented ~30° on each side of the radial direction toward the tangential direction. The cladding material was typically ~70% cold worked and stress relieved. As a result of the stress-relief treatment, the material was partially recrystallized. In addition to the unirradiated archive fuel cladding from the two reactors, another lot of Zircaloy-4 and recrystallized low-oxygen zirconium, both in the

unirradiated state, were analyzed to compare the characteristics of artifact hydride and oxide formation with those of the irradiated materials.

Specimen Preparation

The optical microscopy, scanning electron microscopy (SEM), TEM, and high-voltage electron microscopy procedures have been described elsewhere.¹³ A 20-mm-long "clamshell" was cut from the specimen section of the irradiated Zircaloy cladding in the hot cell. The TEM disks were jet-thinned in electrolyte solutions of perchloric acid, butylcellosolve, and methanol (volume ratio 2:12:30) maintained at -70°C in a dry ice-methanol bath. 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 100 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 camera lengths of the microscopes were calibrated independently. Reflections from the matrix were used as standards to find an exact camera length for each diffraction pattern.

RESULTS

Artifact Surface Oxides and Hydrides

Surface oxide was a predominant artifact phase formed on the low-oxygen unirradiated Zr specimens during preparation of the thin-foil TEM specimens. The surficial nature of the artifact oxide particles could be readily detected from the technique of through-focus microscopy.¹⁶ By changing the imaging condition from underfocus to overfocus in a bright field, the relatively uniform distribution of particles 5 to 10 nm in size changed from black to white contrast (Fig. 1). The contrast change is characteristic of surface particles.^{14,16} The oxide particles also produced a characteristic mottled

background in a bright-field image. Analysis of the diffraction patterns and dark-field imaging showed that the surface particles were tetragonal (lattice constant $a_0 = 0.507$ nm, $c_0 = 0.516$ nm) rather than cubic ($a_0 = 0.5135$ nm) or monoclinic ($a_0 = 0.5145$ nm, $b_0 = 0.5208$ nm, $c_0 = 0.5311$ nm, $\beta = 99.23^\circ$) ZrO_2 phase. The surficial nature of the oxide particles could be also verified from the examination of dark-field stereopairs which can be obtained by means of the " $2\frac{1}{2}$ D-microscopy" technique.¹⁷

For all TEM specimens (i.e., irradiated or unirradiated low-oxygen Zr, Zircaloy-2, or -4), artifact hydrides were present on the specimen surface. For either irradiated or unirradiated Zircaloy specimens, hydride was the predominant artifact surface phase rather than oxide. Diffraction patterns and dark-field morphologies characteristic of the surface hydrides, which are commonly observed in the irradiated Zircaloy specimens, are shown in Fig. 2. Characteristic diffraction patterns similar to those in Fig. 2 have been also reported by other investigators for Zr-Nb alloys¹⁸⁻²⁰ and Zr²¹ specimens. The diffraction patterns of Fig. 2 correspond to a tetragonal structure (lattice constants $a_0 = 0.522$ nm and $c_0 = 0.514$ nm) with an ordered array of solute atoms which give rise to the superlattice reflections. Zaluzec analyzed a surface film in a (111) orientation of the tetragonal structure by the electron energy loss spectroscopy technique, and showed the absence of any oxygen in the phase.¹⁹ The analysis, therefore, strongly indicates that the surface film is an ordered hydride. The diffraction patterns that contain the superlattice reflections are not compatible with the γ zirconium hydride, in which the hydrogen atoms occupy the tetrahedral sites of the unit cell in an ordered manner. However, recent evidence shows the existence of a nonequilibrium hydride with ordered hydrogen occupying octahedral as well as the tetrahedral sites.²² On the basis of the above information, it is

concluded that the surface film is a variant of metastable zirconium hydride. This metastable surface hydride has been designated χ -hydride in this investigation. As a general rule, observation of the characteristic superlattice reflections such as those in Fig. 2 indicates the presence of surface hydride on the specimen. Morphology of the surface hydride is shown in the dark-field image of Fig. 2(D), which was obtained from a (010) superlattice reflection of the surface hydride. When a dark-field image obtained from such superlattice reflections is well focused at magnifications higher than $\sim 50,000\times$, the image reveals irregular-shaped morphology of the surface hydride. More often the irregular-shaped surface hydride particles are clustered to form continuous surface patches or films.

In contrast to the dark-field morphology imaged from a superlattice reflection, a similar image obtained from a fundamental reflection of the surface hydride usually contains spherical- or oval-shaped particles of ~ 5 nm in size in addition to the irregular-shaped surface hydride particles or clusters. An example of such dark-field images is shown in Fig. 2(E), which was obtained from a ($2\bar{2}0$) reflection of the χ hydride. Since the (100) zone axis of cubic ZrO_2 will manifest a diffraction pattern virtually identical to Fig. 2(A) without the superlattice reflections, it is tempting to dismiss such spherical- or oval-shaped particles simply as an artifact surface oxide particle of cubic structure. However, the characteristic reflections of the cubic ZrO_2 have been observed in a consistent manner in association with bulk zirconium hydride primarily in thin-foil specimens which were excised from brittle-failure regions of the irradiated cladding section. This led to a suspicion of a correlation between the brittle mechanical failure and the precipitation of cubic- ZrO_2 and hydride phases. Subsequently, a systematic examination to determine the nature of the precipitates has been undertaken.

Bulk Precipitates of δ Hydride and Cubic ZrO_2

Typical examples of microstructures obtained from thin-foil specimens which were excised from brittle-failure regions of irradiated and mechanically fractured cladding sections are shown in Fig. 3. Those regions were typically 2 to 10 mm away from the actual fracture surface, which was brittle in nature and exhibited a large extent of pseudocleavage characteristic of a pellet-cladding interaction failure. In the bright-field image of Fig. 3(A), a dark contrast of a second phase 30 to 100 nm in size is noticed. Analysis of diffraction characteristics showed that the area contained surface χ -hydride, δ -hydride, and cubic- ZrO_2 phases in addition to the α -Zr matrix. An indexed selected-area diffraction (SAD) pattern is shown in Fig. 3(B). Reflections of the cubic ZrO_2 were diffuse and those of the δ hydride were relatively sharp. Since the reflections from the χ hydride and cubic ZrO_2 are located at virtually identical positions, it was not possible to infer the relative intensity of the reflections of the two phases. However, superlattice reflections such as $(\bar{1}10)_\chi$ and $(1\bar{1}0)_\chi$ of Fig. 3(B) show the presence of the surface χ hydride.

To determine the nature of the cubic- ZrO_2 and δ -hydride phases manifested in the SAD pattern, dark-field experiments were conducted. A very useful technique for discernment of a bulk phase from a surface phase (such as the χ -hydride) is " $2\frac{1}{2}$ D" microscopy.¹⁷ When the dark-field image is slightly overfocused and underfocused in TEM, a slight difference in the angles of the electron passage occurs. Therefore, the two images can be used effectively as stereopairs. By viewing the resulting micrographs with a stereoscope, a bulk and a surface phase can be discerned with this technique. Examples of dark-field stereopairs are shown in Fig. 3(C) and (D). The images of Fig. 3(C) were produced with $(1\bar{1}3)$ reflections of the cubic ZrO_2 as well as the

χ -hydride. The two reflections are located at virtually identical spots. However, a stereoview of Fig. 3(C) clearly shows the bulk nature of the cubic- ZrO_2 precipitates and the surficial nature of the χ -hydride phase. The cubic- ZrO_2 particles shown in Fig. 3(C) have a diameter of ~ 5 nm and in some cases are aggregated in the form of curved threads as indicated by the arrows. By switching the stereopair left and right under the stereoscope, the bottom and top surfaces come into view can be also switched. In this way, it can be readily identified which particle is in the midsection and which particle is either on the top or bottom surface. For example, the particle denoted by the "D" circle in Fig. 3(C) is located on the bottom surface, and the particle denoted by "B" circle is approximately 120 nm above the "D" particle in the midsection of the thin-foil region of ~ 250 nm in thickness. The diffuse film near the lower right corner is located on the top surface. The curvilinear images denoted by the "C" arrows are also bulk phase of clustered cubic- ZrO_2 particles. Dark-field images of δ hydride are not visible in Fig. 3(C), but visible in Fig. 3(D) as nearly spherical or slightly elongated lumps 30 to 100 nm in size. The bulk nature of these hydrides can be clearly discerned from a stereoview examination of Fig. 3(D) (e.g., hydride lump denoted by " γ " arrow). The bulk and surficial phases that are observed in the stereoviews of Figs. 3(C) and (D) are illustrated schematically in Figs. 3(E) and (F), respectively. Although the exact nature of the surface film (oxide, hydride, or hydrocarbon) such as that depicted in Fig. 3(F) is not conclusive, it is not of too much concern in this study because of its artifact nature. However, examination of the " $2\frac{1}{2}$ D" stereopairs such as those of Fig. 3 conclusively show the presence of bulk cubic- ZrO_2 particles and δ -hydride lumps both of which are not artifact phases.

Another example of stereopairs of dark-field images that reveal the

nature and morphologies of the cubic ZrO_2 and the bulk δ -hydride is shown in Fig. 4. Particle-like or curvilinear morphologies of the bulk cubic ZrO_2 are again visible in Fig. 4(C). The cubic- ZrO_2 particles in Figs. 4(C) and (D) are more or less uniformly distributed in depth between the top and bottom surfaces of the thin-foil region. This indicates a homogeneous nature of the precipitation. The cubic- ZrO_2 particles are not visible under the normal bright-field imaging condition. Their presence can be detected only through the weak-beam dark-field $2\frac{1}{2}\text{D}$ -microscopy technique as demonstrated in Figs. 3 and 4.

The bulk hydride shown in Figs. 3(D) and 4(D) is not the same as the long δ -hydride stringers (~ 50 nm wide and ~ 1000 nm long) that can be resolved metallographically in most of the irradiated or hydrided Zr alloys.²³ Indeed the long δ -hydrides were observed in the present irradiated Zircalloys with their characteristic $(10\bar{1}0)_\alpha$ habit plane.²⁴ The smaller hydrides similar to those of Figs. 3 and 4 have been reported for unirradiated Zr and Zr alloys, although the nature (i.e., bulk vs artifact surface) of the hydrides has been in confusion.²⁴⁻²⁶ In spite of the confusion, it seems clear that one cannot assume in general that small-size hydrides are always artifact surface hydrides. In their investigation of orientation of hydrides in Zr, Bedford and Miller²⁴ showed that the small slightly elongated surface hydrides were always characterized by the $(0002)_\alpha$ habit plane. Because of the basal habit plane, the elongated axis of the small hydrides were aligned parallel to a single direction in a grain. In contrast, the long bulk hydrides exhibited $(10\bar{1}0)_\alpha$ habit planes, which resulted in several different directions $\sim 120^\circ$ apart in a given grain. The small hydrides revealed in the dark-field images of Figs. 3(D), 4(D), and (5) exhibit a slightly elongated morphology. Furthermore, as shown in the figures, the elongated axis is oriented in

several different directions. Analysis of the directions showed that they are parallel or nearly parallel to the trace of $(10\bar{1}0)_\alpha$, Fig. 5. Thus, the habit planes observed for the small hydrides in this study are identical to those of the bulk hydrides analyzed by Bedford and Miller. This characteristic is consistent with the stereographic verification of the bulk nature of the small hydrides. This, in turn, confirms further the bulk nature of the cubic-ZrO₂ particles that are usually observed side by side with the small hydrides in comparable depths.

Another type of surface film (round-like patches) is shown in Fig. 5. In the bright-field image of Fig. 5(A), the surface patches with a characteristic mottled appearance (similar to a strawberry) are strongly visible. Such contrasts can be easily mistaken for small hydrides. The small hydride and cubic-ZrO₂ particles are not visible in the bright-field image. However, they are clearly visible in the dark-field stereopairs of Fig. 5(B), which were produced from reflections containing $(11\bar{1})$ of cubic ZrO₂, δ hydride, and surface χ hydride. Again, the bulk nature of the small δ -hydride and cubic-ZrO₂ particles is evident. A careful comparison of the bright- and dark-field images of Fig. 5(A) and (B) shows that the patch-like surface film, visible in 5(A), is different from the small δ hydrides visible in 5(B). A stereoview examination of Fig. 5(B) clearly shows that the faint images of the patch-like films (e.g., the parallel patches marked by the larger arrows) are on the top surface. The images denoted by the smaller arrows are located on the bottom surface. Figure 5 illustrates that an analysis of small hydrides can be misleading if only the bright-field imaging is conducted.

Zr₃O Precipitates

TEM-HVEM examination of thin-foil specimens obtained from regions adjacent to ductile-failure sites of irradiated Zircaloy cladding 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 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. Careful examination of the corresponding SAD patterns of regions containing the dislocation substructures frequently showed superlattice reflections of the Zr₃O phase. The superlattice reflections were diffuse and extremely weak, and could not be detected on the microscope screen. They could be detected only through a careful examination of developed negatives of SAD patterns. Because of the difficulty of detecting the superlattice reflections on the microscope screen, dark-field images from the superlattice reflections could not be obtained. A careful examination of the dark-field images of the dislocation substructure (i.e., substructures in the brittle-failure regions) which were obtained from the (0002) reflection in 1-MeV HVEM revealed that fine particles 2 to 6 nm in size decorated the dislocations. Resolution of the fine particles on the dislocations was possible only from weak-beam dark-field images obtained from the HVEM. This is probably because of the reduced inelastic scattering of the 1-MeV electrons compared to the 0.1-MeV electrons in conventional TEM. Figure 6 shows an example of the SAD pattern containing the superlattice

reflections and (0002) dark-field images showing the dislocations decorated by the fine particles. On the basis of the characteristics demonstrated in Fig. 6 as an example, it is believed that the dislocations in the brittle-failure regions are actually decorated by the Zr_3O precipitates of 2 to 6 nm in size. However, because of the isostructural nature of the Zr_3O and α -Zr matrix (i.e., fundamental reflections of Zr_3O identical to those of α -Zr), conclusive evidence for this could be obtained only through an observation of dark-field images of the superlattice reflections that decorate the dislocation substructures.

In limited cases, Zr_3O superlattice reflections were sufficiently intense to be detected on the microscope, and thereby dark-field images were obtained. An example of the indexed SAD pattern containing such superlattice reflections are shown in Fig. 7(A). Figure 7(B) shows dark-field stereopair images of the Zr_3O phase, which were obtained from the superlattice reflection $(\bar{1}10\bar{1})_{Zr_3O}$ of Fig. 7(A). Stereoview examination of Fig. 7(B) clearly shows the bulk nature of the agglomerated Zr_3O precipitates and surficial nature of artifact χ hydrides.

During the dark-field experiments, it was noticed repeatedly that the intensity of selected Zr_3O superlattice reflections decreased with time during imaging with 0.1-MeV electrons in the JEOL 100 CX-II STEM. The lower intensities are indicative of a smaller degree of ordering of the oxygen atoms. The decreased ordering of the oxygen atoms indicates that the Zr_3O phase was unstable when subjected to beam heating during the 0.1-MeV TEM examination. However, a similar decrease in the intensity of the superlattice reflections was not observed during examination in a 1-MeV HVEM. This can be explained as follows: The kinetic energy of the 1-MeV electrons during the HVEM examination is spent primarily in producing radiation-induced defects.

In contrast, the kinetic energy of the 0.1-MeV electrons during the conventional TEM experiments is absorbed by the specimens, primarily through interaction with phonons, and the result is a significant beam-heating effect. Therefore, great care is necessary to avoid beam heating when imaging the Zr_3O superlattice reflections in a conventional TEM.

Zr-Fe-Cr and Zr-Fe-Ni Intermetallic Precipitates

The major precipitates in the as-fabricated (unirradiated) Zircalloys are the intermetallic phases $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ and $\text{Zr}_2(\text{Fe}_x\text{Ni}_{1-x})$. These precipitates have been known to play an important role in the corrosion resistance of unirradiated Zircalloys in laboratory tests. For example, a fine distribution of small-size intermetallics in β -quenched Zircalloys leads to superior resistance to nodular corrosion. However, stability of the intermetallics is not well understood for in-reactor service conditions. Decomposition of the intermetallics has been reported by Cheng et al.² after irradiation in the Winfrith Steam Generating Heavy Water Reactor. Similar decomposition or decimation of the $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ precipitates was apparent from our examination of the H. B. Robinson Zircaloy cladding, which had been irradiated to a fluence of $\sim 4.4 \times 10^{21} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$). In contrast to this observation, a limited number of the precipitates were present in the Big Rock Point cladding, which had been irradiated to a fluence of $\sim 3.3 \times 10^{21} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$). Figure 8 shows an example of hcp $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ precipitates in a cladding sample from the Big Rock Point fuel bundle. No such precipitates could be observed in the H. B. Robinson cladding. When the specimen of Fig. 8 was heated to $\sim 560^\circ\text{C}$ in the HVEM during 1-MeV electron irradiation, a copious amount of the $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ precipitate formed.

Evidence that $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ precipitates in α -annealed Zircaloy-4 decompose totally after a fluence of $8 \times 10^{21} \text{ n/cm}^2$ ($E > 1 \text{ MeV}$) has been

reported.²⁷ This fluence is approximately twice as large as that for the H. B. Robinson cladding specimen. The large difference in the fluence required for total decomposition of the intermetallic precipitates may be due to the difference in the average flux of fast neutrons in the reactors in which the fuel rods were irradiated (the H. B. Robinson reactor is a PWR, whereas the irradiation of Ref. 27 was presumably carried out in a heavy-water-moderated reactor).

DISCUSSION

The small (30 to 100 nm) bulk δ hydrides shown in Figs. 3 to 5 for the irradiated fuel cladding specimens are evidently a different type of hydride which cannot be observed metallographically. The hydrides are similar in size and orientation to the small hydrides observed by Bedford and Miller²⁴ by TEM for unirradiated Zr specimens. They observed that when a string of small hydrides were oriented in directions close to the trace of $(10\bar{1}0)_\alpha$, the overall shape appeared to be similar to those of the long (~1000 nm) hydrides that are commonly resolved by optical microscopy. The observation of these small bulk hydrides both in irradiated and unirradiated specimens shows that the hydrides were formed thermally.

However, the observation of the bulk cubic-ZrO₂ precipitates in the irradiated specimens of spent-fuel cladding can be explained only in terms of an irradiation-induced phase transformation. The morphology and distribution of the cubic-ZrO₂ particles indicate that the irradiation-induced transformation was homogeneous in nature. The fact that the cubic-ZrO₂ precipitates were usually observed in association with the small bulk δ hydrides indicates a possible role of the hydride precipitation in triggering the homogeneous transformation. Thermal precipitation of the hydrides in the local region could have enriched the nearby α -Zr matrix with oxygen atoms,

which would not dissolve in the hydride, and as a result, would migrate to the nearby matrix. This oxygen enrichment could promote or trigger the irradiation-induced precipitation of the cubic-ZrO₂ particles. Besides the local oxygen content, several factors are considered critical in irradiation-induced precipitation of the cubic-ZrO₂ precipitates, i.e., temperature, dose rate (irradiation flux), and local density of sinks such as dislocations, grain boundaries, and other defects. The mechanism of homogeneous irradiation-induced precipitation has been attributed to amplification of solute (e.g., oxygen) concentration fluctuations on a microscopic scale as a result of enhanced recombination of irradiation-induced vacancies and interstitials in the solute-rich regions.^{28,29} Basic to the coupling of oxygen concentration fluctuations to the irradiation field is the interaction between the oxygen and irradiation-induced defects. Because of the interaction (or trapping), an oxygen concentration heterogeneity induces a redistribution of the irradiation-induced defects. Mutual recombination of the irradiation-induced point defects will then be more active in those regions where the defects tend to accumulate. As a result of the higher rate of mutual recombination, an effective defect sink is generated surrounding the oxygen concentration heterogeneity. Since the point defects are being created at a uniform rate in the Zircaloy specimen in reactor, a flux of irradiation-induced defects will be sustained toward the region of higher defect recombination rate, i.e., the region of oxygen concentration heterogeneity. The latter defect flux then may drag oxygen to further amplify the oxygen concentration fluctuation, and this may lead eventually to a precipitation of the cubic-ZrO₂ particles. The potential of interaction between oxygen and the irradiation-induced defects appears to be maximum in the temperature range of 300 to 350°C on the basis of the temperature dependence of the strain aging⁷

and radiation-anneal hardening⁸⁻¹⁰ behavior of neutron-irradiated Zircaloy-2. This appears also consistent with the observation of the cubic-ZrO₂ precipitates in the spent-fuel Zircaloy cladding specimens which were irradiated at reactor operating temperatures of 290 to 330°C.

The exact nature of the Zr₃O precipitates is not conclusive at this time (i.e., homogeneous vs heterogeneous precipitation), although there are indications of preferential precipitation of the phase on dislocation entanglements (e.g., Fig. 6). Similar ordered structures involving nonmetallic elements such as O and N in unirradiated V, Nb, Ti, and Zr are commonly observed after low-temperature, long-term heat treatments in some atmospheres. Thus, Zr₃O precipitates observed in this study would be classified as an irradiation-enhanced precipitation. In fact, the Zr₃O precipitates may be a precursor phase to the cubic-ZrO₂ precipitates. Apparently the Zr₃O phase is unstable at higher temperatures (e.g., >500°C) since weakening of the superlattice reflections was commonly observed under the beam heating conditions. However, the in-reactor performance of the Zircaloy fuel cladding at ~300°C will be influenced profoundly by the irradiation-induced precipitation of the Zr₃O and/or cubic-ZrO₂ phases. A lower oxygen content in the as-fabricated cladding material or minimization of oxygen and hydrogen uptake during reactor operation would be effective in suppressing irradiation-induced precipitation, and hence, would mitigate embrittlement by precipitation of these phases.

CONCLUSIONS

1. Two types of precipitates involving oxygen were shown to be bulk phases in neutron-irradiated Zircaloy-2 and -4 spent-fuel cladding by means of weak-beam dark-field $2\frac{1}{2}$ D-microscopy technique. They are cubic-ZrO₂ and Zr₃O precipitates.

2. The cubic-ZrO₂ precipitates were nearly spherical in morphology and ~5 nm in size. The precipitates were formed via homogeneous irradiation-induced precipitation, usually in association with bulk hydrides 30 to 100 nm in size. Thermal precipitation of the hydrides is believed to increase the oxygen concentration in the nearby α -Zr, and hence, promote irradiation-induced precipitation in the local region. The Zr₃O precipitation is irradiation-enhanced in nature and may be a precursor transformation for the nucleation of the cubic-ZrO₂ precipitates.
3. The irradiation-induced precipitation of the cubic-ZrO₂ and Zr₃O phases could significantly influence the hardening and embrittlement of the Zircaloy fuel cladding during in-reactor service. Improvements in fuel rod fabrication to reduce oxygen and hydrogen uptake, particularly at the cladding inner surface where stress is expected to be largest, could suppress irradiation-induced precipitation and thereby minimize the potential for embrittlement of the cladding.

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REFERENCES

1. Proc. Seventh Intl. Conf. on Zirconium in the Nuclear Industry, Strasbourg, France, June 24-27, 1985, American Society for Testing and Materials, in press.
2. Cheng, B., Adamson, R. B., Bell, W. L., and Proebstle, R. A., Proc. Intl. Symp. on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, August 22-25, 1983, Myrtle Beach, SC, p. 274.
3. Chung, H. M., *ibid.*, Second Symp., September 9-12, 1985, Monterey, CA, in press.
4. Williams, C. D. and Ells, C. E., Philosophical Magazine, Vol. 18, 1968, p. 763.
5. Coleman, C. E., Gilbert, R. W., Carpenter, G. J. C., and Weatherly, G. C., Phase Stability During Irradiation, Holland, J. R., Mansur, L. K., and Potter, D. I., eds., The Metallurgical Society of AIME, New York, 1977, pp. 587-599.
6. Zee, R. H., Rogerson, A., Carpenter, G. J. C., and Watters, J., Journal of Nuclear Materials, Vol. 120, 1984, pp. 223-229.
7. Veevers, K. and Rotsey, W. B., Journal of Nuclear Materials, Vol. 27, 1968, p. 108.
8. Snowden, K. U. and Veevers, K., Radiation Effects, Vol. 20, 1973, pp. 169-174.
9. Onchi, T., Kayano, H., and Higashiguchi, Y., Journal of Nuclear Materials, Vol. 88, 1980, pp. 226-235.
10. Onchi, T., Kayano, H., and Higashiguchi, Y., Journal of Nuclear Materials, Vol. 116, 1983, pp. 211-218.

11. 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.
12. Lee, D. and Koch, E. F., Journal of Nuclear Materials, Vol. 50, 1974, p. 162.
13. Chung, H. M., in Proc. Intl. Symp. on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, August 22-25, 1983, Myrtle Beach, SC, pp. 297-333.
14. Jostsons, A., Kelley, P. M., and Blake, R. G., Journal of Nuclear Materials, Vol. 66, 1977, pp. 236-256.
15. Northwood, D. O., Gilbert, R. W., Bahen, L. E., Kelley, P. M., Blake, R. G., Jostsons, A., Madden, P. K., Faulkner, D., Bell, W., and Adamson, R. B., Journal of Nuclear Materials, Vol. 79, 1979, pp. 379-394.
16. Northwood, D. O., and Gilbert, R. W., Journal of Australian Institute of Metals, Vol. 18, 1973, p. 158.
17. Bell, W. L., Journal of Applied Physics, Vol. 47, 1976, p. 1676.
18. Stiegler, J. O., Houston, J. T., and Picklesimer, M. L., Journal of Nuclear Materials, Vol. 11, 1964, p. 32.
19. Zaluzec, N. J., "An Analytical Electron Microscope Study of the Omega Phase Transformation in a Zirconium-Niobium Alloy," ORNL/TM-6705, Oak Ridge National Laboratory, June 1979.
20. Harnandez, O. G. and Potter, D. I., in Proc. of AIME-TMS Symp. on Phase Stability During Irradiation, Pittsburgh, PA, October 5-9, 1980, pp. 601-612.
21. Ploc, R. A., Journal of Nuclear Materials, Vol. 28, 1968, pp. 48-60.

22. Petrunin, V. F., Dolukhanyan, S. K., Zemlyanov, M. G., and Marchenko, S. V., Soviet Physics of Solid State, Vol. 23, 1981, 1126.
23. Ells, C. E., Journal of Nuclear Materials, Vol. 28, 1968, pp. 129-151.
24. Bedford, A. J. and Miller, D. R., Journal of Australian Institute of Metals, Vol. 17, 1972, pp. 120-123.
25. Bailey, J. E., Acta Metallurgica, Vol. 11, 1963, pp. 267-280.
26. Arunachalam, V. S., Lehtinen, B., and Östberg, G., Journal of Nuclear Materials, Vol. 21, 1967, pp. 241-248.
27. Cheng, B. and Adamson, R. B., "Mechanistic Studies of Zircaloy Nodular Corrosion," in Ref. 1.
28. Cauvin, R. and Martin, G., Journal of Nuclear Materials, Vol. 83, 1979, pp. 67-78.
29. Martin, G., Cauvin, R., and Barbu, A., in Phase Transformations During Irradiation, Ed. F. V. Nolfi, Jr., Applied Science Publishers, 1983, pp. 47-74.

Fig. 1. Characteristic Black (A) to White (B) Contrast Change in Bright-Field Images of Surface Oxide Particles Formed on Low-oxygen Unirradiated Zr TEM Specimen Upon Changing from Underfocus (A) to Overfocus (B).

Fig. 2. Characteristic Diffraction Patterns and Dark-Field Morphologies of the Artifact Surface Hydrides Observed on Irradiated and Unirradiated Zircalloys. (A) (100) orientation of the hydride, (B) (A) superimposed on (10 $\bar{1}$ 0) of α -Zr, (C) (A) superimposed on (12 $\bar{3}$ 1) of α -Zr, (D) dark-field image from (010) of the surface hydride, and (E) dark-field image from (2 $\bar{2}$ 0) of the surface hydride and cubic oxide. Subscripts α and χ in diffraction patterns denote α -Zr and surface χ hydride, respectively.

(C)

Fig. 2. (Contd.)

Fig. 3. Typical TEM Micrograph Containing Bulk δ -Hydrides and Cubic- ZrO_2 Precipitates in spent-fuel Irradiated Zircaloy-2 Specimens. (A) Bright-field image, (B) indexed selected-area diffraction pattern, (C) and (D) dark-field image stereopairs obtained from the $(1\bar{1}3)$ and $(\bar{2}2\bar{2})$ reflections, respectively, of the cubic ZrO_2 , bulk δ -hydride, and surface χ -hydride. Subscripts α , C, γ , and χ in (B) denote, respectively, α -Zr, cubic ZrO_2 , δ hydride, and surface χ hydride. (E) and (F) show schematically the distributions of the phases visible in (C) and (D), respectively.

(C)

(D)

Fig. 3. (Contd.)

BULK
CUBIC ZrO_2

SURFACE X-HYDRIDE

SURFACE X-HYDRIDE

3 (E)

3 (F)

Fig. 4. TEM Micrographs Similar to Fig. 3. (A) Bright-field, (B) indexed SAD pattern, (C) and (D) dark-field stereopairs obtained from $(2\bar{2}0)$ and $(1\bar{1}\bar{1})$ reflections of the cubic ZrO_2 , bulk δ hydride, and surface χ hydride.

4(c)

4(D)

5 (A) & (B)

Fig. 5. HVEM Micrographs Similar to Figs. 3 and 4. (A) Bright-field image showing mottled surface oxide or hydride patches and (B) same area as (A) showing dark-field image stereopair of $(11\bar{1})$ reflections of cubic ZrO_2 , δ hydride, and surface χ hydride. The mottled surface patches

Fig. 6. HVEM Micrographs Obtained from Regions of Zircaloy-4 Cladding Irradiated in the H. B. Robinson Reactor. (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 to 6 nm in size; (D) dark-field image similar to (C) but from another nearby dislocation substructure. Subscripts α , s, χ , and c in the SAD pattern denote, respectively, α -Zr, Zr₃O, surface χ -hydride, and cubic-ZrO₂ phases. The letter D denotes multiple diffraction spots.

Fig. 6. (Contd.)

7 (A) (B)

Fig. 7. TEM Micrographs Obtained from Zircaloy-2 Cladding Tube Specimen Irradiated in the Big Rock Point Reactor. (A) SAD pattern showing Zr_3O fundamental and superlattice reflections; (B) dark-field stereopair obtained from the $(110I)_{Zr_3O}$ superlattice reflection showing the bulk nature of the precipitate.

8 A1(B)(C)

Fig. 8. $\text{Zr}(\text{Fe}_x\text{Cr}_{1-x})_2$ Precipitate Observed in Zircaloy-2 Spent-Fuel Cladding after a Fuel Burnup of 22 MWd/kg U. (A) Bright-field image; (B) dark-field image; and (C) SAD pattern. Subscripts α and H refer to Zr matrix and the hcp precipitate, respectively.