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ABSTRACT

Precipitates in high-burnup (>20 MWd/kg U) Zircaloy spent-fuel cladding discharged from commercial boiling- and pressurized-water reactors have been characterized by TEM-HVEM. Three classes of primary precipitates were observed in the irradiated Zircaloys: Zr_3O (2-6 nm), cubic-ZrO_2 (≤10 nm), and δ-hydride (35-100 nm). The former two precipitations appear to be irradiation induced in nature. $Zr(Fe_xCr_{1-x})_2$ and $Zr_2(Fe_xNi_{1-x})$ intermetallics, which are the primary precipitates in unirradiated Zircaloys, were largely dissolved after the high burnup. It seems, therefore, that the influence of the size and distribution of the intermetallics on the corrosion behavior may be quite different for the irradiated Zircaloys.

INTRODUCTION

Precipitates in Zircaloy fuel cladding are known to play an important role in the mechanical and corrosion properties of the material. For example, it has been well established that the size and distribution of the Zr-Fe-Cr and Zr-Fe-Ni intermetallics play an important role in the nodular corrosion resistance of unirradiated Zircaloys.[1] Although precipitates in as-fabricated unirradiated Zircaloys are well documented and may have implications for the performance of the unirradiated fuel cladding, similar information on irradiated material is very limited. During 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.[2] It is also possible that some precipitates normally stable without irradiation are no longer stable under irradiation and may undergo dissolution into the matrix. The purpose of this paper is to report on some TEM observations of several precipitates contained in Zircaloy-2 and -4 irradiated either by neutrons in power reactors or by electrons in a high-voltage electron microscope (HVEM). The observations are compared with those for unirradiated material.

EXPERIMENTAL PROCEDURES

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 to 28 MWd/kg U and 3.3 to 4.4 x 10^{21} n/cm^2 (E >0.1 MeV), respectively. 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 STEM or in a Kratos/AEI-EM7 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 difrraction patterns obtained from the HVEM are far more accurate than those from conventional microscopes. The camera lengths of the microscopes were calibrated independently. Reflections from the α-matrix were used as standards to find an exact camera length for each diffraction pattern. In-situ irradiation with 1-MeV electrons was conducted in the HVEM in a vacuum of ~1.3 x 10^{-4} Pa at 300 to 600°C.

Zr-Fe-Cr AND Zr-Fe-Ni INTERMETALLICS

The predominant intermetallics observed in the as-fabricated archive materials were fcc and hcp $Zr(Fe_xCr_{1-x})_2$ in the Zircaloy-4 and the $Zr(Fe_xCr_{1-x})_2$ and tetragonal $Zr_2(Fe_xNi_{1-x})$ in the Zircaloy-2. However, for the H. B. Robinson cladding with a burnup of ~28 MWd/kg U, the $Zr(Fe_xCr_{1-x})_2$ precipitates were dissolved during the in-reactor irradiation. Analyses of TEM specimens obtained from several different fuel rods showed no $Zr(Fe_xCr_{1-x})_2$ precipitates in the H. B. Robinson cladding. The $Zr_2(Fe_xNi_{1-x})$ precipitates in the Big Rock Point reactor Zircaloy-2 were also largely dissolved after a burnup of ~22 MWd/kg U. In the Zircaloy-2

material, only a very limited number of hcp $Zr(Fe_xCr_{1-x})_2$ precipitates (a_o = 0.508 nm, c_o = 0.828 nm) could be detected (Fig. 1). It appeared that only a few oversize $Zr(Fe_xCr_{1-x})_2$ precipitates survived the in-reactor irradiation and most of the smaller ones dissolved. Figure 2 shows the morphology of the hcp $Zr(Fe_xCr_{1-x})_2$ intermetallics that precipitated during 1-MeV electron irradiation in the HVEM at 560°C. No fcc form of the precipitates was observed in the annealed Zircaloy-4.

Zr_3O PRECIPITATES

The Zr_3O precipitates, viz., an ordered Zr-O phase exhibiting superlattice reflections,[3,4] were primarily observed in association with dislocation substructures of the irradiated cladding tubes that failed in a brittle manner. Very fine Zr_3O precipitates, 2-6 nm in size, decorating individual dislocations could be observed by HVEM.[3] Figure 3(A) shows a SAD pattern containing the characteristic superlattice and primary reflections of the Zr_3O phase. The dark-field stereopair images of Fig. 3(B), which were obtained from the superlattice reflection $(\bar{1}10\bar{1})_{Zr_3O}$ of Fig. 3(A), reveal the bulk Zr_3O precipitates and artifact surface χ-hydrides.[4] The stereopair was obtained by a "$2\frac{1}{2}$D-microscopy" technique.[5]

CUBIC-ZrO_2 PRECIPITATES

The cubic-ZrO_2 phase, normally stable at $\geq$1580°C without irradiation, was also identified in the irradiated Zircaloy-2 and -4. The phase has an fcc fluorite structure with a lattice constant of 0.5135 nm. Morphologically, the cubic-ZrO_2 precipitates were either spheres <10 nm in size or short linear aggregations of the spheres. The precipitates were frequently observed with Zr_3O or δ-hydride precipitates 40 to 100 nm in size. An indexed SAD pattern and dark-field stereopair are shown in Figs. 4(B) and 4(C), respectively. A stereoview examination of Fig. 4(C) reveals the bulk nature of both forms of cubic-ZrO_2 precipitates.

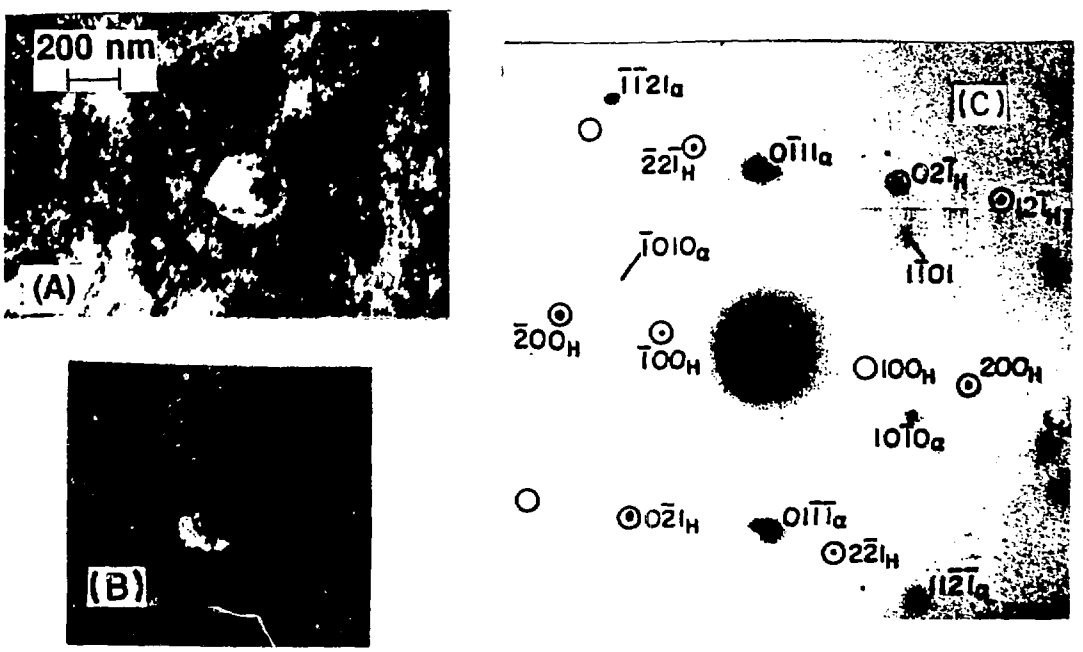

Fig. 1. $Zr(Fe_xCr_{1-x})_2$ Precipitate Observed in Zircaloy-2 Spent-Fuel Cladding after a Fuel Burnup of 22 MWd/kg U. (A) Bright-field image; (B) dark-field image; and (C) SAD pattern. Subscripts α and H refer to Zr matrix and the hcp precipitate, respectively.

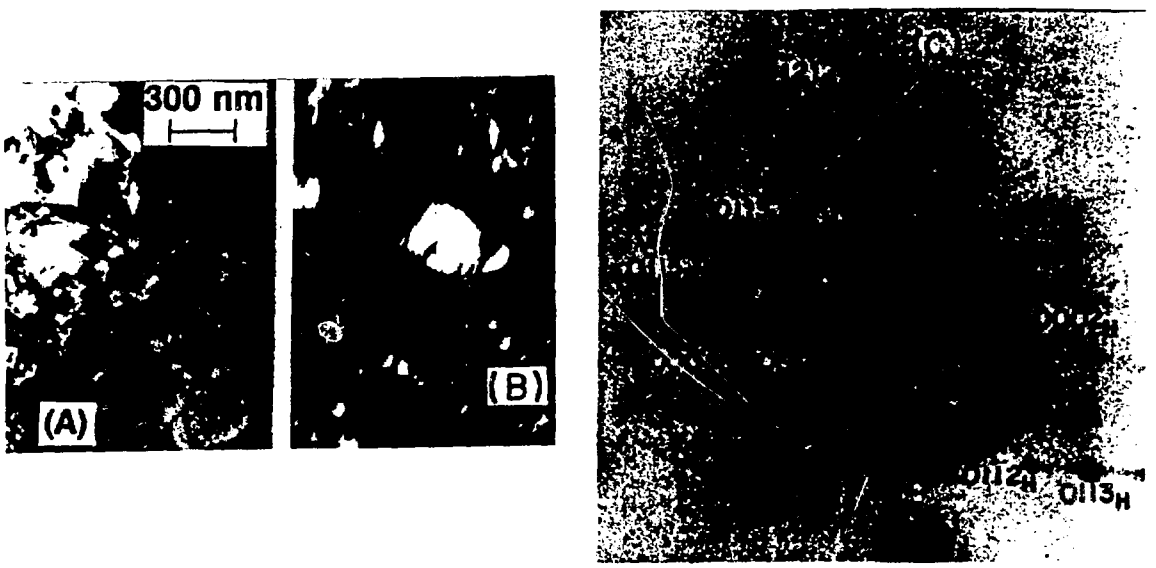

Fig. 2. Precipitates Similar to Those of Fig. 1, Produced During 1-MeV Electron Irradiation of the Zircaloy-2 Spent-Fuel Cladding at 560°C.

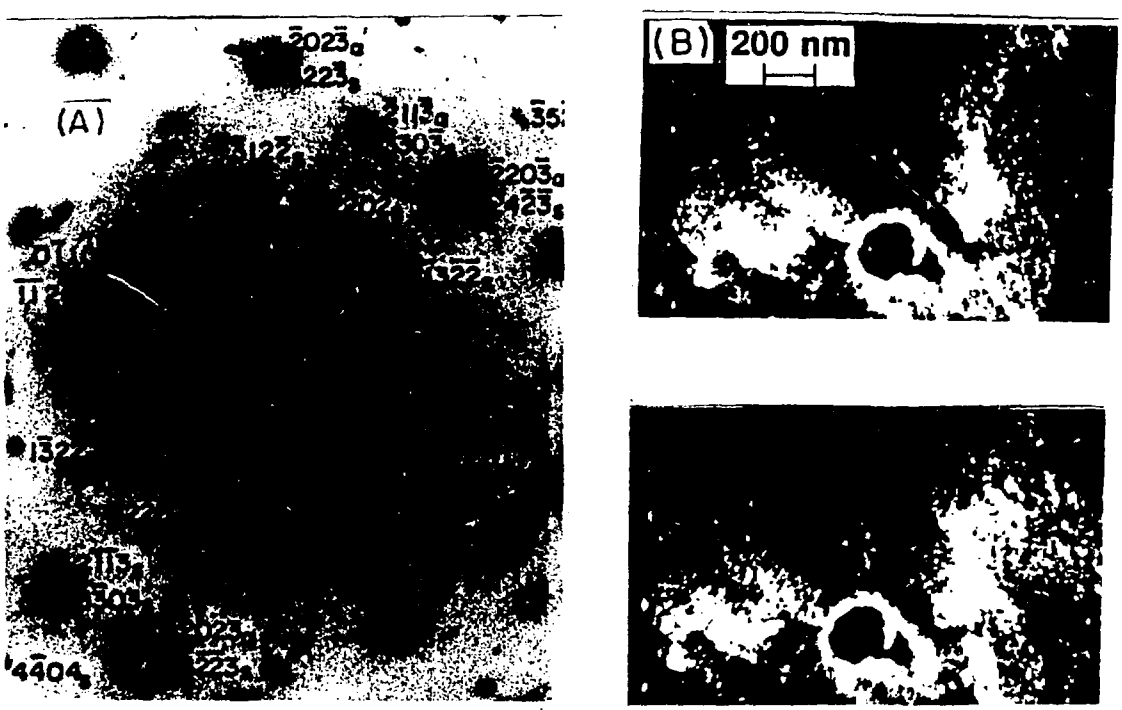

Fig. 3. SAD Pattern (A) and Dark-Field Stereopair (B) Showing Zr_3O Precipitates in Zircaloy-2 Spent-Fuel Cladding. Subscript s in (A) denotes the Zr_3O reflections.

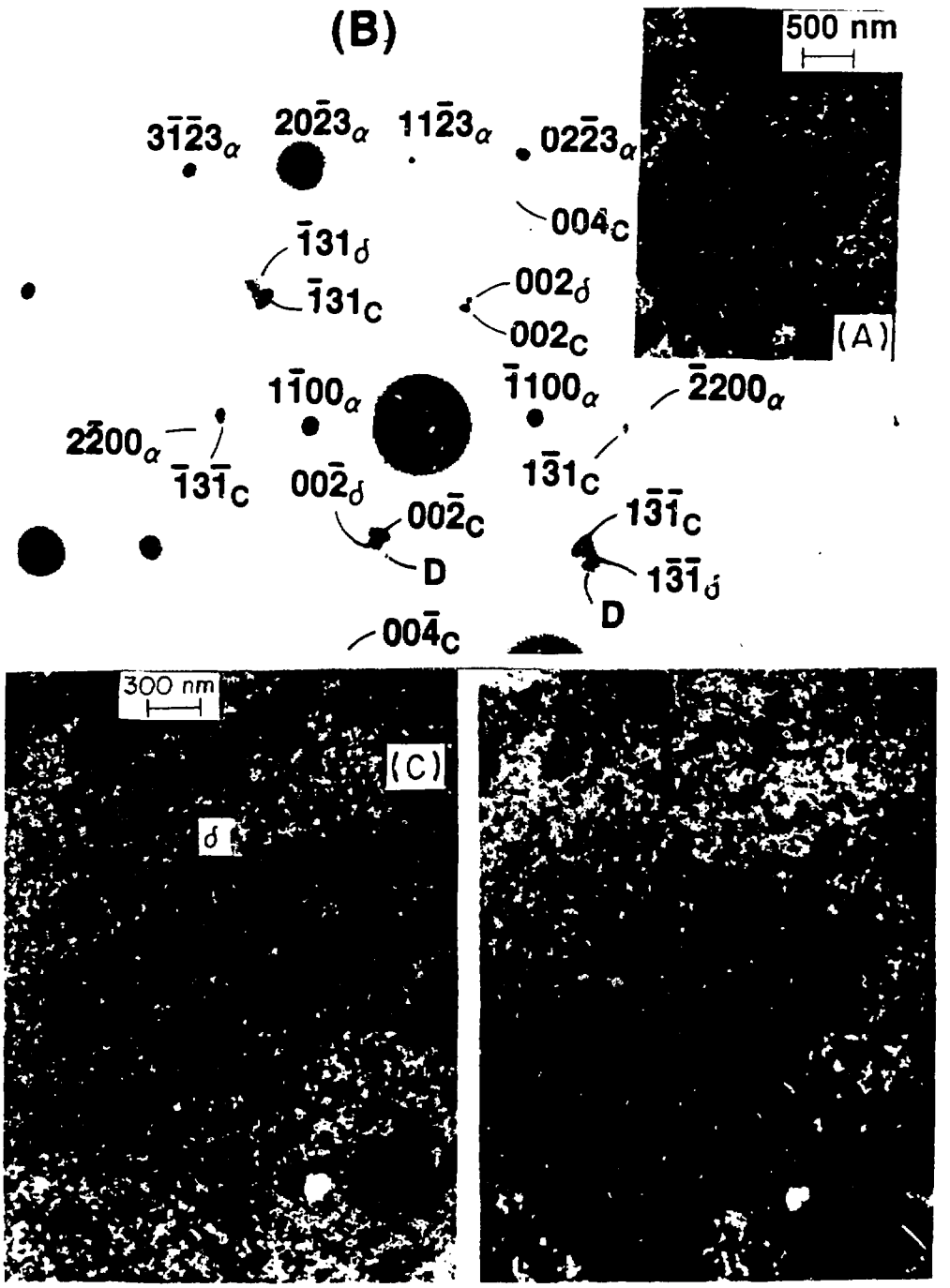

Fig. 4. HVEM Micrographs Obtained from Zircaloy-4 Spent-Fuel Cladding Showing Cubic-ZrO_2 and δ-Hydride Precipitates. (A) Bright-field image; (B) SAD pattern; and (C) dark-field stereopair from (002) reflections of the cubic-ZrO_2 (subscript C) and δ-hydride (subscript δ) precipitates. Letter D denotes double-diffraction spots.

In-situ irradiation of the spent-fuel cladding specimens with 1-MeV electrons in the HVEM at 325°C in a vacuum of ~1.3 x 10^{-4} Pa resulted in irradiated-induced precipitation of both cubic-ZrO_2 and Zr_3O phases. Dark-field images and an SAD pattern obtained after the electron irradiation are shown in Fig. 5. An SAD pattern taken from the same region at room temperature prior to the heating did not show reflections of appreciable intensities of either phase. The in-situ irradiation experiment confirms the radiation-induced nature of precipitation of the cubic-ZrO_2 and Zr_3O phases.

δ-HYDRIDE

The fcc (a_o = 0.4778 nm) δ-zirconium hydride was frequently observed in association with the cubic-ZrO_2 precipitates, as shown in Fig. 4. The bulk hydride was ellipsoidal or nearly spherical in shape and ~35 to 100 nm in size. The bulk hydrides shown in Fig. 4 are different from the long (~1000 nm) δ-hydride stringers commonly observed metallographically in irradiated cladding. The smaller hydrides similar to those of Fig. 4 could be observed only by TEM. The hydrides formed thermally but not by radiation-induced precipitation.

Zr_3Si PRECIPITATES

Zirconium silicides, like the Zr-Fe-Cr and Zr-Fe-Ni intermetallics, were present in minor amounts in the spent-fuel cladding. An example of the silicides is shown in Fig. 6. SAD patterns of several different zones of the precipitate were obtained through a tilting experiment. The analysis of the SAD patterns showed the precipitate to be the tetragonal (a_o = 1.101 nm, c_o = 0.545 nm) Zr_3Si phase.

CONCLUSION

Three major classes of precipitates were observed in Zircaloy-2 and -4 cladding irradiated in power reactors: Zr_3O (2-6 nm), cubic-ZrO_2 (~10 nm), and δ-hydride (35-100 nm). Some $Zr(Fe_xCr_{1-x})_2$, $Zr_2(Fe_xNi_{1-x})$, and Zr_3Si precipitates were also observed, but only in minor quantities. This is in distinct contrast to unirradiated Zircaloys, in which the $Zr(Fe_xCr_{1-x})_2$ and $Zr_2(Fe_xNi_{1-x})$ intermetallics are the major precipitates. It seems, therefore, that the influence of the size and distribution of the intermetallics on the corrosion behavior may be different for the irradiated Zircaloys. Formation of the brittle Zr_3O and cubic-ZrO_2 precipitates under irradiation may also influence the oxidation behavior. These factors require further investigation.

ACKNOWLEDGMENT

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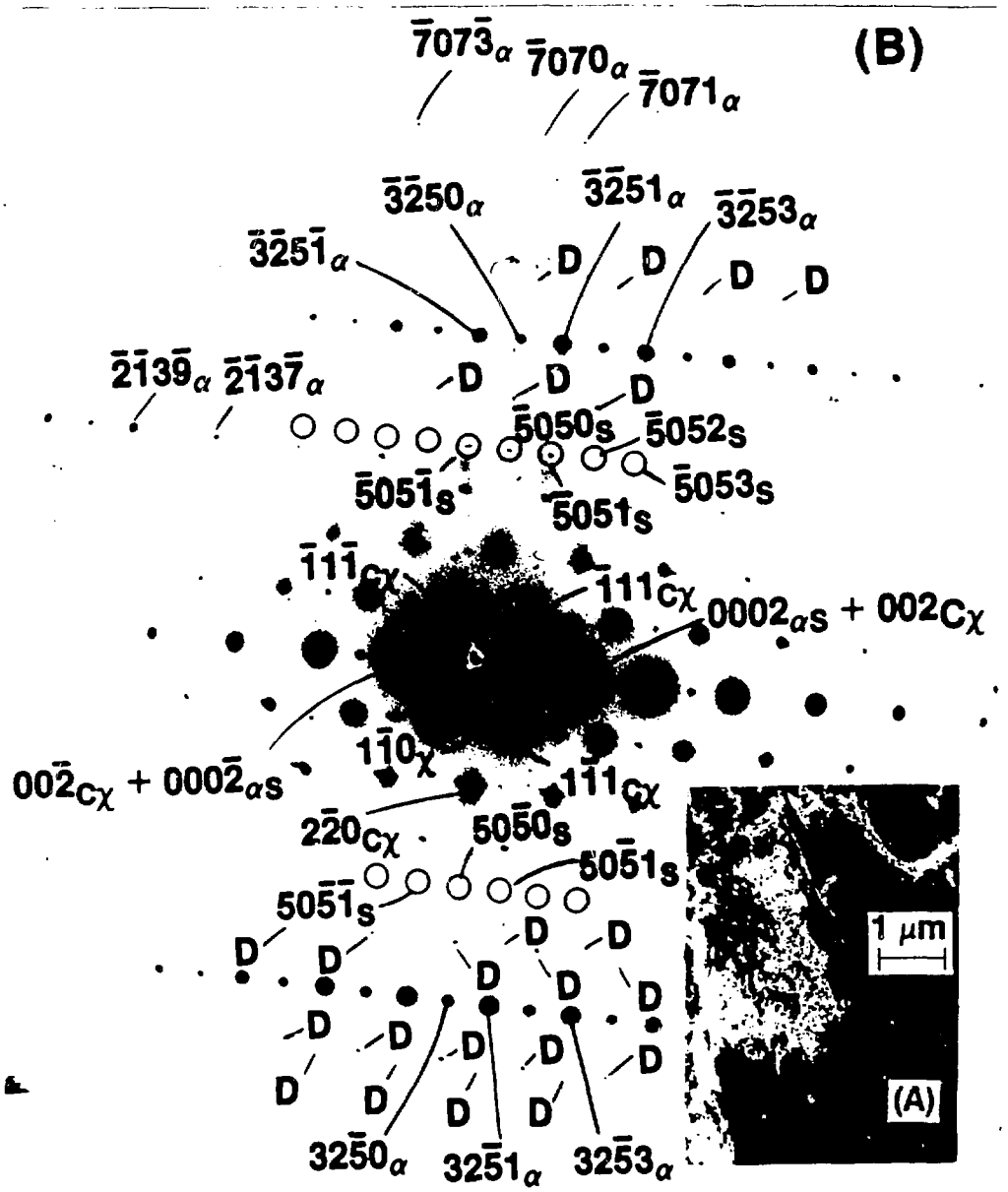

Fig. 5. HVEM Micrographs Obtained at Room Temperature after 1-MeV Electron Irradiation of a Thin-Foil Specimen of Zircaloy-4 Spent-Fuel Cladding at 325°C in Vacuum. (A) Bright-field image; (B) SAD pattern showing (110) zone of the cubic ZrO_2 and circled superlattice reflections from the Zr_3O; (C) dark-field image from the (002) of the cubic ZrO_2 and (0002) of the Zr_3O and α-Zr; and (D) dark-field image from the $(\bar{1}11)$ of cubic ZrO_2. Subscript χ refers to artifact surface-hydride reflections.

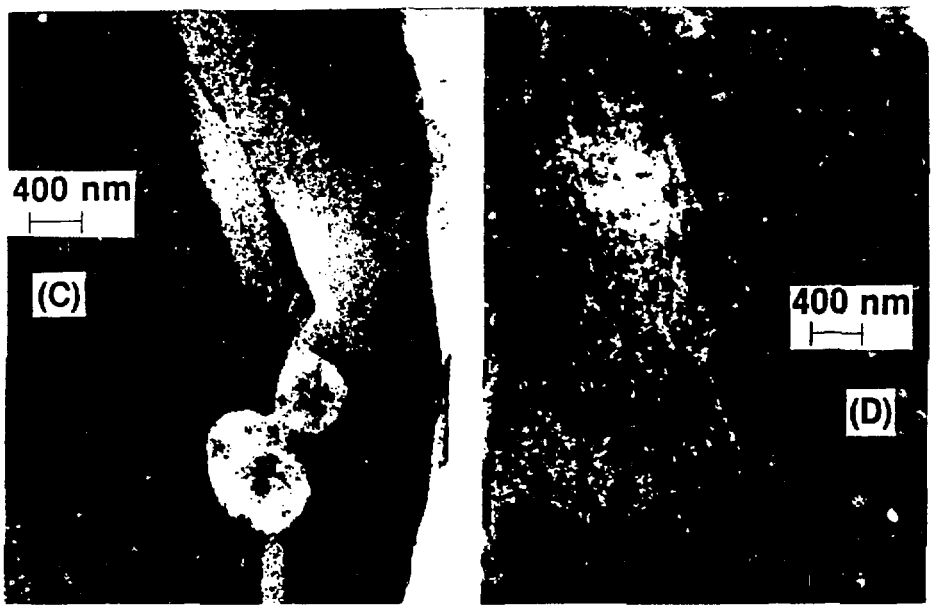

Fig. 5. (Contd.)

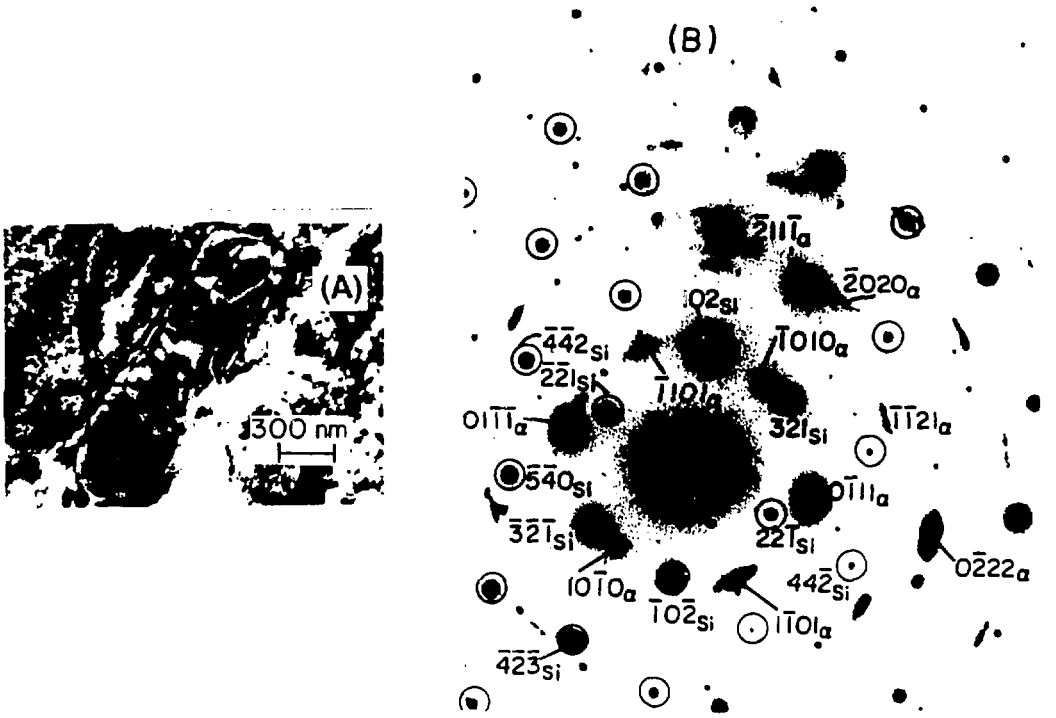

Fig. 6. Bright-Field Image (A) and SAD Pattern (B) of a Zr_3Si Precipitate (subscript Si) Observed in Zircaloy-4 Spent-Fuel Cladding.