

DISCUSSION

B. D. Warr¹ (written discussion)—Following aqueous exposures (250 to 360°C, pH 10.5) at Ontario Hydro (in-reactor and out-reactor) of Zircaloy-2 and Zr-2.5 Nb, we have observed hydrides at the metal-oxide interface by SIMS sputtering through the oxides. However, the oxidation rate appears to be independent of the presence of hydrides at the interface. Do you have an explanation for this?

A. M. Garde (author's closure)—In order to observe the corrosion rate acceleration due to hydrides as proposed in this paper, significant amounts of hydrides *localized* at the metal-oxide interface are necessary. You may want to re-examine your data regarding the extent and location of hydrides. If lithium is added to the coolant, its effect on the proposed mechanism also needs to be evaluated. We have not evaluated the effect of lithium on the proposed mechanism. Also, the effect of hydrides on the oxidation rate appears to be a function of hydride precipitate size, orientation, and distribution. These factors need to be evaluated for your data. As shown by the results of our investigation, the duration of the corrosion test used to evaluate the effect of hydrides should be long enough to avoid interference from surface-related effects.

C. K. Chow² (written discussion)—At temperatures above 300°C, the hydrides seem to be ductile and would not crack under stress. (Delayed hydride cracking does not occur.) This is also supported by a poster paper by Bai et al. at this symposium. (The mechanical properties at 350°C were not influenced by hydrogen concentration up to 1000 ppm.) Your results showed that hydride cracking might occur up to 420°C. Would you comment on this?

A. M. Garde (author's closure)—When mechanical properties of zirconium alloy components with hydride precipitates are measured, one is actually subjecting a composite of metal phase and hydride phase to deformation. In such a test crack propagation through the metallic ligament is generally important. Because of the ductile metallic matrix, such a composite is more ductile than the hydride phase alone. For the corrosion rate acceleration discussed in the present paper, crack initiation at the hydride is the important step. Crack propagation is relatively unimportant. The ductility parameter important for the corrosion rate acceleration is the ductility of the hydride phase, not that of the composites. In the temperature region of 300 to 420°C, delayed hydrogen cracking is not observed as a result of the ductility of the alpha-zirconium matrix. The observation is not related to the ductility of zirconium hydride.³

V. F. Urbanic⁴ (written discussion)—If your model for enhancement in corrosion due to hydride precipitation and failure at the metal-oxide interface is correct, it should be independent of the bulk water chemistry of the corrosion environment. For uniform oxidation in high oxygen water conditions in-reactor, accelerations over and above that due to oxygen

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³Northwood, D. O. and Kasasih, U., "Hydrides and Delayed Hydrogen Cracking in Zirconium and Its Alloys," *International Metals Reviews*, Vol. 28, No. 2, 1983, pp. 92–121.

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alone are rarely seen, even when the hydrogen content of the base metal is sufficiently high for hydrides to be present. Can you comment on this in view of your proposed mechanism for corrosion acceleration?

A. M. Garde (author's closure)—The proposed mechanism contributes to the corrosion rate acceleration only when hydride precipitation is favored at the metal-oxide interface (i.e., under low oxygen coolant conditions). Under high dissolved oxygen conditions of the coolant, the liberated hydrogen will prefer to combine with the excess oxygen rather than going to the metal. With oxidizing coolant conditions, the hydride precipitation in the metal is discouraged; therefore the corrosion rate acceleration associated with the hydride precipitation and fracture is not expected to be observed. The mechanism of oxidation under high-oxygen coolant environment may be different from that for a low-oxygen coolant environment. The proposed mechanism is applicable to the low-oxygen coolant environment.

S. K. Yagnik⁵ (written discussion)—Your conclusion that the heat flux driven migration of H_2 to oxide/metal interface further promotes the oxidation rate appears to be a *mechanistic* explanation of the heat flux effect on the corrosion rate (such as was discussed in the paper by Billot and Giordano, pp. 539–565). Would you comment on this?

A. M. Garde (author's closure)—Billot and Giordano addressed the effect of heat flux on the oxygen diffusion through the barrier oxide layer. In our paper we have discussed the effect of heat flux on the concentration of hydride precipitates at the metal-oxide interface where the new oxide is forming. The net affect of the heat flux on the corrosion process will probably include both of the aforementioned factors.

D. O. Northwood⁶ (written discussion)—The author quoted our work (Northwood et al.) as supporting a hydride-enhanced corrosion correlation. This work (on Zr-2.5Nb) merely demonstrated that an enhanced corrosion rate was associated with an enhanced hydriding rate. The interpretation was that in the post-transition region the oxide became less protective both with respect to further oxidation and the ingress of hydrogen.

A. M. Garde (author's closure)—The observed association between the enhanced corrosion rate and the enhanced hydriding rate is consistent with the “feedback” mechanism of corrosion rate enhancement due to hydride precipitation proposed in the present paper.

B. Cox⁷ (written discussion)—I thought that we had resolved the question of the effects of hydrogen concentration in Zircaloy on the corrosion behavior many years ago, and found no effect if solid hydride layers were absent from the surface. We did three types of experiments:

1. We varied the thickness of otherwise identical specimens so that the TSS for hydrogen was reached at different times in the oxidation curve. We saw no effect of this precipitation on the kinetics.
2. We added different amounts of hydrogen to samples and varied the surface preparation. Pickled specimens apparently showed an effect of hydrogen concentration, specimens polished to give smooth surfaces did not. Electron microscopy showed oxide cracking around etched out hydrides to be the source of the effect.

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3. When studying iodine SCC we found that hydrides in the specimen surfaces could be already cracked at the start of the experiment; these could be revealed by a short oxidation as fingers of penetrating oxide.

I suggest that your experiments are confirming these early observations.

A. M. Garde (author's closure)—In high burnup PWR fuel cladding, the metal side of the metal-oxide interface is often like a solid hydride layer. In order to evaluate the effect of hydrides on the in-PWR corrosion rate, the following conditions appear to be important for the autoclave testing to achieve good correlation: test temperature of 633 K, test duration long enough to avoid interference from the surface preparation effects, and water (and not steam) environment at high pressure rather than atmospheric pressure. Some of the factors affecting the results described in Refs 4 to 6 are likely to be: (a) use of steam environment, (b) test temperature of 773 K in some cases, (c) short duration of autoclave test, and (d) steam pressure of 1 atm. Moreover, the effect of hydrides on the corrosion rate depends on the hydride precipitate size, orientation, and distribution. Information on these parameters is not available in the work referred to above. Our observations on long term (>300 days in autoclave) corrosion testing show that thin wall specimens show higher corrosion rates than thick wall specimens. This observation is consistent with the model proposed in the present paper.

R. B. Adamson⁸ (written discussion)—What is the origin of the radial hydrides in the test specimen that showed the highest corrosion?

A. M. Garde (author's closure)—Few radial hydrides were observed only in the *recrystallized* Zircaloy-4 specimen. Apart from the habit plane preference, alpha-alpha grain boundaries also provide preferential sites for hydride precipitation. In a recrystallized microstructure, some grain boundaries are oriented perpendicular to the tube outside surface and thereby favor precipitation of few radial hydrides. The recrystallized Zircaloy-4 specimen, however, did not show highest corrosion among the specimens tested.

J. C. Clayton⁹ (written discussion)—Your micrograph was an excellent example of a pronounced hydride gradient. However, our examinations of irradiated LWBR core rods (Zry-4 [RXA & SRA], ThO₂-UO₂ fuel pellets, NH₃OH coolant) and test rods consistently showed uniform hydride distributions, probably because of low temperature gradients and low hydrogen concentrations (≤ 90 ppm). Only in defected irradiated test rods were definite hydrogen gradients observed. What were the hydrogen concentrations in your micrographs that showed the gradients?

A. M. Garde (author's closure)—The extent of hydride precipitate gradient would depend on the value of the temperature gradient across the cladding wall as well as the level of hydrogen concentration. The temperature gradient depends on the heat flux. For the micrograph shown in Fig. 9, the PWR core average heat flux was about 571 000 W/m² (181 000 Btu/h/ft²) and had a local cladding hydrogen concentration of about 300 ppm.

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