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IN ALPHA-ANNEALED ZIRCALOY-4**

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PRESENTED AT THE
EPRI UTILITY-INDUSTRY WORKSHOP
ON
PWR FUEL ROD CORROSION

WASHINGTON, D.C.

JULY 28-30, 1993

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HYDROGEN PICKUP AND REDISTRIBUTION
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ABSTRACT

Zircaloy-4, which is widely used as a core structural material in Pressurized-Water Reactors (PWR), picks up hydrogen during service. Hydrogen solubility in Zircaloy-4 is low and hydrides precipitate after the Zircaloy-4 matrix becomes slightly supersaturated with hydrogen. These hydrides embrittle the Zircaloy-4. To study hydrogen pickup and concentration, a postirradiation nondestructive radiographic technique for measuring hydrogen concentration was developed and qualified. Experiments on hydrogen pickup were conducted in the Advanced Test Reactor (ATR). Out-of-pile tests were conducted to determine the conditions for which hydrogen would migrate. Finally, a phenomenological model was built and indexed to the data. This presentation describes the experiments and the model, presents the results of experiments, and compares the model predictions to experimental results.

INTRODUCTION

Zircaloys were developed at the Bettis Atomic Power Laboratory to improve corrosion resistance and mechanical properties over those of zirconium (1). During service, Zircaloys also pickup hydrogen, primarily from hydrogen that is liberated as part of the oxidation of Zircaloy by water (2). Hydrogen in solution will diffuse down a thermal gradient and concentrate in cold regions of Zircaloy components (3). Due to hydrogen's low solubility in Zircaloys, zirconium hydrides form at relatively low concentrations of hydrogen, especially on cooling to near room temperature. These hydrides are very brittle and significantly degrade the mechanical properties of Zircaloys. This change in properties must be understood and incorporated into design evaluations. Specifically, fundamental data and models that describe hydrogen pickup and redistribution must be available to optimize light-water-reactor nuclear fuel designs. Therefore, in-reactor and out-of-reactor experiments were conducted to provide the database for a fundamental model that provides insight into the phenomena involved and that supports development of design procedures.

HYDROGEN PICKUP

To support model development, hydrogen pickup was measured on alpha-annealed Zircaloy-4 coupons that were irradiated in the Advanced Test Reactor (ATR). A nondestructive method of measuring hydrogen content was developed and qualified. This method measured the neutron attenuation by absorbed hydrogen as a neutron beam passed through a specimen (Figure 1). The attenuation of the beam was calibrated to the hydrogen content of Zircaloy by the use of standards. Since the method was nondestructive, interim measurements were made on coupons using an on-site neutron beam. This allowed the hydrogen pickup of individual samples to be followed as a function of radiation exposure. Out-of-reactor hydrogen pickup was measured after autoclave exposure by destructive hot vacuum extraction to obtain reference data.

Out-of-reactor reference pickup data of Zircaloy-4 coupons from three ingots are shown in Figure 2 for 600°F exposure. Similar in-reactor pickup data are shown in Figures 3 and 4 for exposure at 680°F and 590°F, respectively, for three neutron flux levels: high flux or $\phi > 10^{14}$ n/cm²/sec,* medium flux or 10^{14} n/cm²/sec $> \phi > 10^{13}$ n/cm²/sec, and low flux or $\phi < 10^{13}$ n/cm²/sec. To determine if the hydrogen pickup was correlated with sample oxidation, the measured hydrogen content was plotted as a function of measured oxygen concentration, as determined by weight-gain measurements and as shown in Figures 5 and 6. For normal conditions, the ratio was a function of fluence and temperature but the kinetics of the oxidation reaction could be used to estimate the hydrogen pickup. As discussed below, in-reactor the ratio was a function of oxide thickness. This supported the view that most of the hydrogen absorbed during service was from the oxidation. Further, it supported use of a factor to estimate hydrogen pickup from measured or predicted oxidation.

HYDROGEN CONTENT OF OXIDE FILMS

The hydrogen concentration in the oxide film may be different from the hydrogen concentration in the Zircaloy-4 metal. Several studies have shown this to be the case (References 4-5). High or low hydrogen concentrations in the oxide can have an impact on interpretation of hydrogen measurements to determine $\Delta H/\Delta O$ ratios and hydrogen migration. To determine the impact of this effect, Secondary Ion Mass Spectroscopy (SIMS) was used to determine the concentration profile through the oxide and metal of an autoclaved Zircaloy-4 specimen. The hydrogen profile is shown in Figure 7, in which hydrogen is uniformly dispersed in the oxide and concentrated in hydrides in the metal.

To quantify the hydrogen concentrations in the oxide and metal, autoclaved and in-reactor corrosion coupons were tested for hydrogen concentration, with and without the oxide film, as shown in Figure 8. The results from autoclave specimens, tested at 680°F, 2800 psi in deionized degassed water, are given in Table I. The results from in-reactor testing are shown in Figures 9 and 10. Out-of-reactor samples exhibited similar hydrogen concentrations in the oxide and metal. However, in-reactor samples had oxide hydrogen concentrations that were independent of temperature, flux, and fluence. The in-reactor samples reached a high hydrogen concentration quickly and saturated. Since the oxide hydrogen concentration was independent of exposure, the relative amounts of hydrogen in the metal and oxide depended on sample thickness and exposure.

HYDROGEN MIGRATION IN ZIRCALOY-4

Hydrogen migration down temperature gradients results in a concentration of hydrogen in hydrides when the metal concentrations of hydrogen exceed the solubility in the cold regions of a zirconium alloy. However, hydrogen migration models can not be based on equilibrium, principally because volume mismatch between metal and hydride densities results in lattice distortion on precipitation. The energy required to induce this distortion delays precipitation until the metal hydrogen concentration exceeds the equilibrium concentration. To describe this process an unbalanced precipitation and resolution model was developed, as summarized in Table 2. The metal concentration of hydrogen for equilibrium between metal and hydride was used for dissolution of hydrides. Precipitation of hydrides required a supersaturation of hydrogen in the metal matrix. Qualification experiments were designed to confirm the model and to provide data for indexing constants. To determine the solid-solution diffusion coefficient, diffusion couples were made by precharging half of sheet samples

*All fluences are for E > 1 MeV.

(Figure 11) and annealing the samples at temperatures between 500°F and 900°F, e.g. for 3.9 days at 800°F (Figure 12). The diffusion coefficients determined from these studies are shown in Figure 13, and are in reasonable agreement with the results of Kearns (Reference 6) but below results reported by Someno (Reference 7), Sawatzky (Reference 8), and Mallett and Albrecht (Reference 9). Data in the literature have demonstrated that a hysteresis exists in the precipitation and dissolution solvi (Figure 14). To determine the hydride dissolution solvus, similar diffusion couples were made but the two sides were allowed to come to equilibrium at each temperature (Figure 15). The hydride dissolution solvus as a function of temperature was determined by measuring the postanneal hydrogen concentration of the initially uncharged half of the samples (Figure 16).

To determine the hydride precipitation solvus uniformly-hydrogen-charged specimens were annealed in a temperature gradient that varied linearly and monotonically from one end of each sample to the opposite end (Figure 17). Hydrogen precharge levels were chosen such that the entire sample was in the single-phase state at the beginning of the test. The cold ends of each sample were held at either 500°F, 600°F, 700°F, or 800°F and the temperature gradients were either 300°F/inch or 400°F/inch. Hydrogen diffused down the temperature gradient until it reached a portion of the sample, i.e., a temperature, at which there was a high enough hydrogen concentration to precipitate hydrides. This concentration determined the precipitation solvus, as shown in Figure 18 for the 700°F-cold-end sample. The results from each test are shown in Figure 19, where they are compared with literature data.

The heat of transport, Q^* in equation 1 in Table 2, was determined for each sample from the slopes of $\log ([H])$ vs inverse temperature, e.g., Figure 18 for a 700°F-cold-end sample. The results are shown in Figure 20. The reprecipitation constant, α in equation 2 in Table 2, determines the reprecipitation kinetics in this model and can be determined by measuring the surface and midplane precipitated hydrogen concentration as in Figure 21. Samples were corroded in concentrated lithiated water at temperatures between 550° and 680°F in autoclaves at pressures high enough to maintain temperature below the saturation temperature. The results are shown in Figure 22.

This model for hydrogen diffusion was benchmarked to several out-of-reactor experiments. As illustrated in Figures 23 and 24, the primary conclusion from these benchmarking experiments is that the model over predicts hydrogen segregation to the colder regions. One sample (Figure 23) was placed in a steep temperature gradient and the other sample (Figure 24) was placed in a shallow temperature gradient. After annealing, the samples were sectioned and hydrogen concentrations were measured by hot vacuum extraction. The resulting hydrogen-concentration profiles are shown in Figures 23 and 24, along with the temperature profiles and the model predictions of the hydrogen concentrations. The model predicts the observed concentrations adequately for the steep temperature gradient (Figure 23) but not for the shallow temperature gradient. The most likely cause of the model misprediction is hydrogen trapping at lattice defects. Trapping would result in higher required driving forces, i.e., thermal gradient, to redistribute the hydrogen.

For application to fuel designs, the above migration model must be combined with a model for hydrogen pickup. Based on the discussion in the previous section, the pickup model must properly reflect the relative amounts of hydrogen in the metal and oxide.

CONCLUSIONS

To describe the embrittlement of zirconium alloys due to formation of hydrides, the following aspects must be understood: hydrogen pickup rate, holdup of hydrogen in the oxide,

diffusion rates in a matrix with hydrogen traps, hydrogen concentration in the metal for hydride dissolution, and metal hydrogen concentration for hydride precipitation. The experiments described provide qualification data for each aspect, although additional data are needed in some areas, e.g., on holdup of hydrogen in the oxide. The model described is adequate for steep gradients but overpredicts hydrogen redistribution for shallow temperature gradients. This deficiency is thought to be due to the lack of a description of hydrogen trapping at lattice defects, i.e., binding energies between the hydrogen strain field and lattice defect strain fields.

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TABLE 1
Hydrogen Retained in Oxide
Autoclave Samples

<u>Sample</u>	<u>Sample Thickness</u>	<u>Wt. Gain</u>	<u>Hydrogen Content (ppm)</u>	
			<u>Oxide On*</u>	<u>Oxide Off**</u>
1	.035"	642 mg/dm ²	669 ± 11	660 ± 7
2	.035"	616 mg/dm ²	751 ± 9	750 ± 4
3	.061"	1091 mg/dm ²	574 ± 8	589 ± 6
4	.057"	993 mg/dm ²	558 ± 10	552 ± 6
5	.065"	204 mg/dm ²	177 ± 3	185 ± 6
6	.1136"	1052 mg/dm ²	337 ± 3	338 ± 3

* Measurements of hydrogen concentration in both metal and oxide.

** Measurements of hydrogen concentration in metal only.

TABLE 2
ANALYTICAL MODEL

- I. Hydrogen diffuses through the alpha (hcp) phase in response to temperature and solid solution concentration gradients.

$$\vec{J} = -D \nabla \vec{C} - \frac{DQ * C}{RT^2} \nabla \vec{T}$$

- D - Diffusion coefficient of hydrogen through α Zircaloy
C - Solid solution concentration of hydrogen in α Zircaloy
Q* - Heat of Transport
T - Temperature

- II. Hydrides (if present) dissolve instantaneously to maintain the alpha Zircaloy at solubility.

Hydride precipitates if the alpha Zircaloy is sufficiently supersaturated.

Precipitation is not instantaneous but occurs at a rate proportional to the matrix supersaturation.

$$R_p = \alpha^2 (C - C_{Pr})$$

- R_p - Rate of precipitation
 α - Fitted rate parameter
 C_{Pr} - Concentration at which precipitation occurs

FIGURE 1 HYDROGEN PICKUP METHOD OF MEASUREMENT

I. INERT GAS FUSION OF CORROSION COUPON SECTIONS

II. NEUTRON BEAM ATTENUATION

EXPERIMENTAL ARRANGEMENT FOR NOTCHED
SPECTRUM MEASUREMENTS

FIGURE 2
HYDROGEN PICKUP OF ALPHA-ANNEALED
ZIRCALOY-4 IN 600°F AUTOCLAVE

FIGURE 3
HYDROGEN PICKUP VS TIME (680 F)
ZIRCALOY-4

FIGURE 4
HYDROGEN PICKUP VS TIME (590 F)
ZIRCALOY-4

FIGURE 5
HYDROGEN PICKUP VS OXYGEN WEIGHT GAIN
ZIRCALOY-4

FIGURE 6
HYDROGEN-TO-OXYGEN PICKUP RATIO FOR ALPHA-ANNEALED
ZIRCALOY-4 AS A FUNCTION OF FLUENCE

FIGURE 7 DISTRIBUTION OF HYDROGEN IN OXIDE FILM

680°F WATER FILM

FILM THICKNESS 1 MIL

TRANSVERSE SECTION OF SPECIMEN AS SEEN
IN A 150 μ m FIELD SIMS IMAGE

1H SIMS IMAGE OF A SECOND PORTION OF SPECIMEN #3.
Cs PRIMARY BEAM, 150 MICRON FIELD, 60 SECOND DATA COLLECTION.

FIGURE 8 METHOD OF MEASUREMENT

INERT GAS FUSION OF SAMPLES WITH AND WITHOUT OXIDE FILMS

CONCENTRATION OF OXIDE FILM FOUND AS FOLLOWS

$$C_T (t_m \rho_m + 2t_o \rho_o) = C_m t_m \rho_m + 2C_o \rho_o t_o \quad (1)$$

WHERE C_T -IS THE TOTAL HYDROGEN CONCENTRATION OF THE SAMPLE MEASURED WITH THE OXIDE FILM LEFT ON (PPM BY WEIGHT)
 C_m -IS THE HYDROGEN CONCENTRATION OF THE METAL (PPM BY WEIGHT)
 C_o -IS THE HYDROGEN CONCENTRATION OF THE OXIDE (PPM BY WEIGHT)
 t_m -IS THE BASE METAL THICKNESS (INCHES)
 t_o -IS THE OXIDE FILM THICKNESS (INCHES)
 ρ_m -IS THE DENSITY OF ZIRCALOY (6.545 G/CM³)
 ρ_o -IS THE DENSITY OF THE OXIDE FILM (5.65 G/CM³)

FIGURE 9
OXIDE HYDROGEN CONCENTRATION VS FLUENCE

FIGURE 10
OXIDE HYDROGEN CONCENTRATION VS FILM THICKNESS

FIGURE 11 PREPARATION AND TESTING SEQUENCE OF SAMPLES TO DETERMINE HYDROGEN-DIFFUSION KINETICS AND HYDROGEN SOLVUS

SECTIONING OF DIFFUSION COUPLE FOR HYDROGEN CONCENTRATION ANALYSIS

FIGURE 12
DIFFUSION COUPLE DATA
ZIRCALOY-4, 800°F, 3.9 DAYS

FIGURE 13
DIFFUSION COEFFICIENT OF HYDROGEN
THROUGH ALPHA ZIRCONIUM

FIGURE 14
HYDROGEN SOLVUS OF ZIRCONIUM ALLOYS
RANGE IN LITERATURE DATA AS
FUNCTION OF MEASUREMENT TECHNIQUE

FIGURE 15 **DIFFUSION COUPLE**

FIGURE 16
HYDRIDE DISSOLUTION SOLVUS
OF ZIRCONIUM ALLOYS

FIGURE 17
LINEAR THERMAL GRADIENT SPECIMEN

SECTIONING OF SAMPLE FOR HYDROGEN ANALYSIS

FIGURE 18
ZIRCALOY-4
COLD END AT 700°F, 300°F/ INCH GRADIENT

FIGURE 19
HYDROGEN PRECIPITATION SOLVUS
OF ZIRCONIUM ALLOYS

FIGURE 20
Q* VS TEMPERATURE
ZIRCALOY -4

NOTED TEMPERATURE IS COLD TEMPERATURE IN SAMPLES CONTAINING LINEAR THERMAL GRADIENTS OF 300°F / INCH AND 400°F / INCH

FIGURE 21

METHOD OF DETERMINING α_p

SUPERCHARGING OF ISOTHERMAL CORROSION COUPONS

J_o CONSTANT

C_o CONSTANT

$$M_{ppm} = \frac{J_o \cdot t \cdot l \cdot \alpha}{D^{1/2}} \cdot \frac{\cosh\left(\frac{\alpha x}{D^{1/2}}\right)}{\sinh\left(\frac{\alpha l}{D^{1/2}}\right)}$$

J_o = SURFACE HYDROGEN FLUX
 D = DIFFUSION COEFFICIENT
 l = SPECIMEN HALF THICKNESS
 x = DISTANCE FROM MIDPLANE
 M = QUANTITY OF HYDROGEN PRECIPITATED

$$MX_1 / MX_o = \cosh(\alpha x / D^{1/2})$$

FIGURE 22
PRECIPITATION RATE PARAMETER
VS TEMPERATURE

FIGURE 23
HYDROGEN CONCENTRATION VS POSITION
ANNEALED 30 DAYS SUBJECTY TO INDICATED
TEMPERATURE PROFILE
INITIAL HYDROGEN UNIFORM AT 100 PPM

FIGURE 24
HYDROGEN CONCENTRATION VS POSITION
ANNEALED 200 DAYS UNDER INDICATED TEMPERATURE PROFILE
HYDROGEN PRECHARGED INTO TEST SPECIMEN AT THE 650°F END

**DATE
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