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LETTER TO THE EDITORS

REDISTRIBUTION OF HYDROGEN IN ZIRCALOY

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1. Introduction

During operation of light water reactors (LWRs) Zircaloy fuel cladding tubes pick-up hydrogen. The hydrogen pick-up emanates mainly from the corrosion reaction: $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$ and the hydrogen produced by radiolytic decomposition of water in a radiation field [1].

It has been known for a long time that the hydrogen dissolved in Zircaloy can redistribute in the presence of a temperature gradient to the colder regions. Sawatzky and coworkers [2,3] studied this phenomenon extensively in the 1960s in out-of-pile tests and developed models to describe it. However, Sawatzky's model is not suited to treat conditions that persist in LWRs where the cladding is subjected to radial, axial, and circumferential temperature gradients plus a continuous generation of hydrogen from the cladding's waterside.

When the hydrogen concentration in Zircaloy exceeds its terminal solubility limit, zirconium hydride precipitation occurs. Hydrogen dissolves in the hexagonal closed packed α-phase while the hydride phase consists of a number of subphases with different crystal structures. In the temperature range of 300–400 °C the hydride is said is be in the δ-phase.

In this letter we intend to formulate a model for describing the hydrogen redistribution that can occur in LWR fuel rod cladding in the presence of radial and axial temperature gradients. This model has then been used to elucidate observations of hydrogen redistribution localized close to pellet interfaces in boiling water reactor (BWR) fuel rods.

2. The model

Hydrogen pick-up by the Zircaloy-2 fuel cladding tube in BWRs is assumed to take place uniformly from its waterside by the oxidation process as discussed in the introduction.

The hydrogen pick-up is a function of cladding temperature, fast neutron flux, irradiation time and the material properties of Zircaloy. For the present study, the maximum hydrogen uptake, N_g ($\mu g/dm^2$), for BWR conditions is taken to be a linear function of time:

$$N_g = \text{const.} \times t, \tag{1}$$

where const. = 10.62 and t is the irradiation time in days.

This correlation, which is empirically based, is used to give the hydrogen content in the cladding around pellet interfaces (a few mm in height) in the high hydrogen content regions along a fuel rod. Such regions are most efficiently detected by neutron radiography.

Hydrogen absorbed at the metal-oxide surface diffuses into the Zircaloy lattice due to the presence of a temperature gradient. The governing equation for this process is:

$$\frac{\partial N}{\partial t} = -\nabla \boldsymbol{J}, \tag{2}$$

with

$$\boldsymbol{J} = -D(\nabla N - Q^* N \nabla \beta), \tag{3}$$

where D is the diffusivity, Q^* the heat of transport taken to be 25 100 J/mol (6000 cal/mol), N the hydrogen concentration, $\beta = 1/RT$, T the temperature, R the universal gas constant and ∇ the gradient operator. The time τ, over the distance r, in which the hydrogen reaches a state of equilibrium, can be estimated by

$$\tau \gg \tau_0 = r^2/D. \tag{4}$$

For example at 310 °C, $D = 1.7 \times 10^{-6}$ cm^2/s [3]; and therefore for $r = 2$ mm, $\tau_0 \approx 6.5$ h. This implies that hydrogen diffusion in Zircaloy is so rapid (compared to the hydrogen production rate in the cladding) that we can rightfully assume that hydrogen is always in a state

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of equilibrium. The steady state solution of eq. (2) is obtained by setting $J = 0$, which gives

$$N_e = C \exp(Q^*/RT), \tag{5}$$

where C is a constant determined by the imposed boundary condition. Since the outer surface temperature of the cladding is assumed to be constant, $T = T_0$ ($\beta = \beta_0$), corresponding to a concentration N_u, the concentration in the α-phase can be written

$$N_\alpha = N_u \exp(Q^*(\beta - \beta_0)). \tag{6}$$

Zirconium hydride builds up (the δ-phase) when N_α reaches the terminal solid solubility limit of hydrogen in Zircaloy, N_s, given by

$$N_s = N_1 \exp(-H\beta), \tag{7}$$

where N_1 is a constant, and H is the heat of mixing which is measured from a diffusion experiment [2]. Thus at the (α, δ) boundary $N_\alpha = N_s$, and using eq. (7):

$$H = -RT \ln(N_\alpha/N_1). \tag{8}$$

The heat of mixing is regarded here as a stochastic variable subject to statistical fluctuations. These fluctuations can be due to Zircaloy crystal structure nonuniformities, such as grain boundaries, dislocations or other structural defects generated by irradiation.

Assuming that that the fluctuations of H obey a Gaussian distribution, we can introduce a dimensionless variable, x, defined by

$$x = \frac{H - \langle H \rangle}{\sigma}, \tag{9}$$

where $\langle H \rangle$ is the mean value of the enthalpy corresponding to a single measured point taken to be 34530 J/mol [3], and σ its standard deviation, taken to be 415.8 J/mol K. At the (α, δ)-phase boundary

$$x = \frac{-T \ln(N_\alpha/N_1) - \langle H \rangle/R}{\sigma/R}. \tag{10}$$

We remark that the axial redistribution of hydrogen in the cladding is induced by fluctuations in the enthalpy, or for that matter, the terminal solid solubility, which causes precipitation of hydrogen atoms in the coldest regions rather than by a purely thermal diffusion of the atoms to those regions.

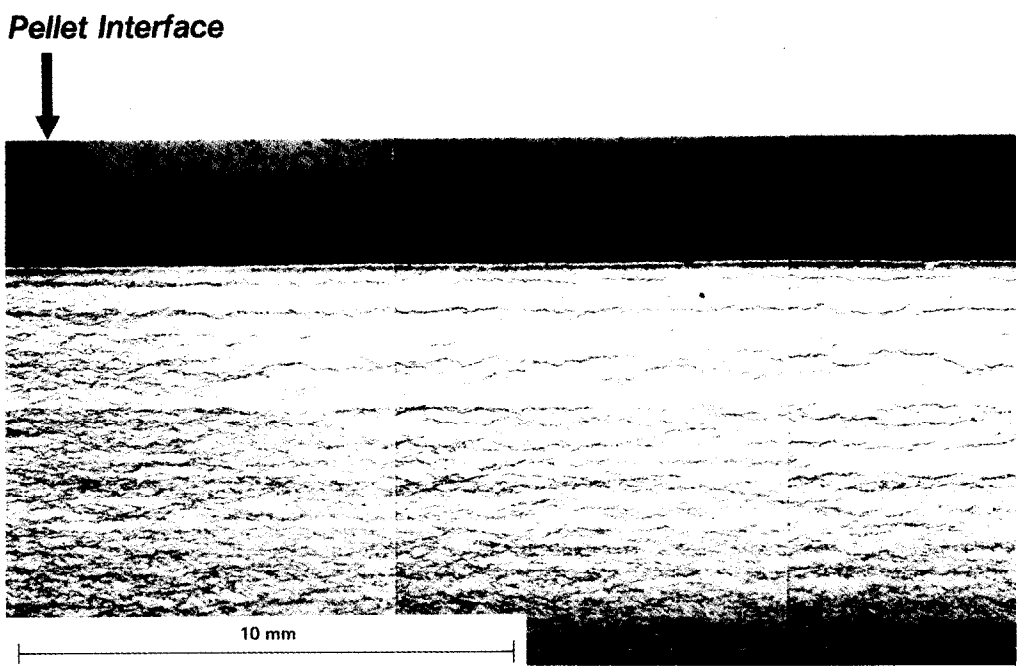

Fig. 1. A portion of Zircaloy cladding near the fuel pellet-to-pellet interface. The fuel operated in a BWR with an end-of-life rod average burnup of about 30 MWd/kg U.

Fig. 1 shows a typical distribution of hydrogen concentration in a BWR cladding along the pellet. It is noticed that the hydrogen concentration increases toward the pellet interface where, due to a large pellet–cladding gap, it is colder than at the mid-pellet region of the cladding. It should be mentioned that detailed chemical analyses have established that hydrogen pick-up did not emanate from the pellet-side of the cladding. This source of hydrogen is removed during fuel rod fabrication by strictly controlling impurities containing hydrogen or elements which produce hydrogen by nuclear reactions.

our aim is to calculate the concentration of hydrogen atoms in the material, as distributed in the α and δ phase. To do this we must first evaluate the fraction (or probability distribution) of hydrogen atoms found in the δ-phase. But the probability of finding hydrogen in the δ-phase, $P(x)$, is given by

$$P(x) = \frac{1}{\sqrt{2}\pi}\int_{-\infty}^{x} e^{-t^2/2}\,dt, \tag{11}$$

where x is defined by eq. (10). This integral can be evaluated by the polynomial and rational approximation of Abromowitz and Stegun [4]. Then the total hydrogen concentration in the material is calculated by the relation:

$$N = [1 - P(x)]N_\alpha + P(x)N_\delta, \tag{12}$$

where N_δ is the hydrogen concentration of the ($\alpha + \delta$, δ)-phase boundary which is taken to be constant after Sawatzky and Vogt [3], $N_\delta \approx 16\,000$ ppm. Now the alert reader notices that the snag in the above theory is that the variable N_u entering P (via x and N_α) is as yet unknown, meaning that it is not given a priori by the basic properties of hydrogen in Zircaloy. However, N must obey the conservation of particles, that is

$$N = N_g, \tag{13}$$

where N_g is given by eq. (1). The unknown variable N_u has been found by solving eq. (13) numerically using Newton's method. More precisely, if

$$f(N_u) = N - N_g, \tag{14}$$

the Newton algorithm is

$$N_u(n+1) = N_u(n) - \frac{f(N_u)n}{(\partial f/\partial N_u)n}, \tag{15}$$

with

$$\frac{\partial f}{\partial N_u} = \left[\frac{1}{\sqrt{2}\pi}e^{-x^2/2}\frac{RT}{\sigma}\left(1 - \frac{N_\delta}{N_\alpha}\right) + (1-P)\right]e^{Q(\beta-\beta_0)}. \tag{16}$$

Note that the calculated concentration variables N_α, N_δ, and N_g are local variables, meaning that they are calculated only at one segment of the tube wall. To find the total radial concentration across the tube wall these variables are integrated.

$$N(z) = \int_0^r N(r')\,dr'. \tag{17}$$

This integration is done by Simpson's rule over 100 radial regions and the resulting concentration is a function of the axial coordinate z. The temperature distribution across the wall is calculated with the aid of a finite difference code in (r, z) coordinates which is used as an input to the above theory.

3. Calculations and results

To determine the temperature distribution values in the cladding wall around a pellet interface, the ABB Atom fuel performance codes STAV-6 and TEMPER were used for a typical 8×8 bundle fuel rod with two different pellet designs in regard to their chamfer sizes, as given in table 1.

The calculations are done for a maximum linear heat generation rate of 288 W/cm typical for a rod in an ABB Atom built reactor with an 8×8 fuel bundle. The cladding wall temperatures are determined for seven radial nodes and twelve axial nodes with the aid of a standard finite difference calculation of the heat equation in (r, z) coordinates. Also, axial symmetry along half of the pellet region is assumed for convenience. The results are presented in figs. 2 and 3 for the two cases. We observe that the temperature in the cladding inner regions sharply decreases towards the pellet interface. In addition, the axial temperature gradient is sharper in case a than in case b.

The temperature distribution values and the theory described above are used to calculate the hydrogen

Table 1
Fuel pellet data

	Case a (mm)	Case b (mm)
Pellet diameter	10.44	10.44
Pellet height	11	11
Chamfer depth	0.25	0.10
Chamfer width	0.70	0.30
Cladding outer diameter	12.25	12.25
Cladding inner diameter	10.65	10.65

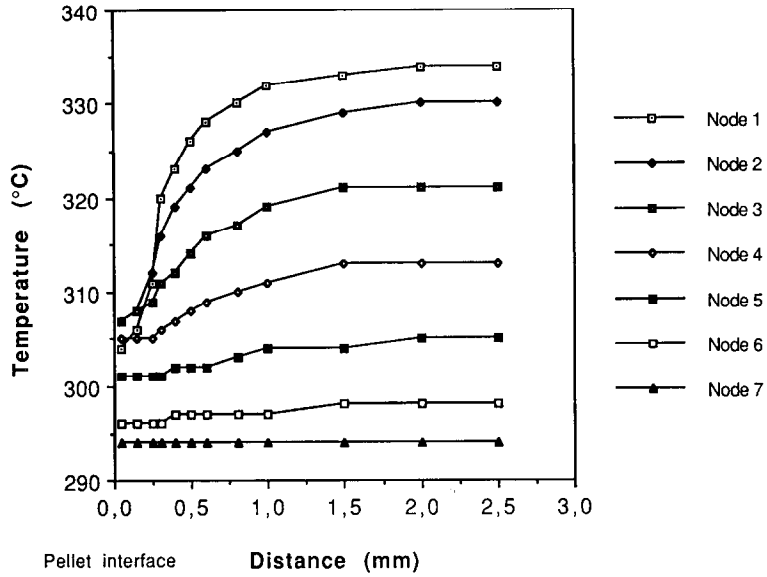

Fig. 2. Calculated axial temperature along a Zircaloy cladding tube at different radial slices (nodes). The geometry is "case a" as given in table 1.

distribution in the cladding. The temperature at the outer surface of the cladding is fixed at $T_0 = 567$ K and the radial variation is fitted by

$$T(r) = T_0 + \frac{r}{R}(T_i - T_0), \tag{18}$$

where T_i is the cladding inner surface temperature and r the distance across the wall.

The results of our calculations are presented in fig. 4 for cases a and b. As can be seen, a lower axial temperature gradient in case b at the pellet interface

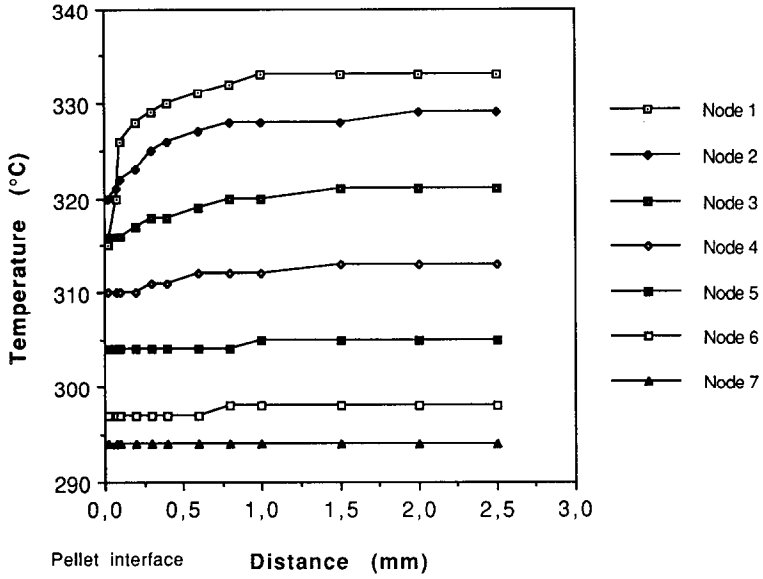

Fig. 3. Calculated axial temperature variation along the cladding at different radial slices (nodes). The geometry is "case b" as given in table 1.

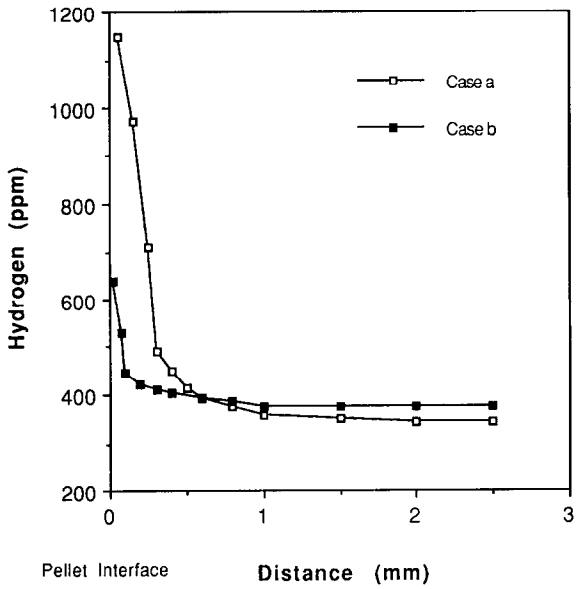

Fig. 4. Comparison between the axial redistribution of hydrogen in Zircaloy cladding for the two cases with different geometries. The curves are generated by using the theory described in the text.

region, by about 10 K/mm at the cladding inner surface, results in a lower hydrogen concentration in that region of the order of 500 parts per million (ppm) locally after 1900 days of reactor operation. Note that according to the hydrogen uptake correlation, the average hydrogen content in the considered cladding region is roughly 380 ppm.

The outcome of our analysis is that pellet chamfer size can have an appreciable impact on hydride localization in the cladding at pellet interface regions. Reducing the size of the chamfer will be one remedy for mitigating this effect.

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