

## Hydrogen Redistribution Due to Temperature Gradients in Zirconium Alloys—a Finite Element Approach

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### Abstract

The finite element method is used to determine the temperature redistribution due to pressure tube/calandria tube contact, and the resulting hydrogen<sup>1</sup> migration leading to the growth of blisters in pressure tubes. The fundamental equations governing the diffusion of hydrogen in zirconium alloys are re-formulated so that a single set of equations are used throughout both the single-phase (solid solution) and the two-phase (hydride and solid solution) regions. The model considers the complex three-dimensional geometry near the pressure tube/calandria tube contact, the anisotropy of the hydrogen/deuterium diffusion coefficients and the complex thermal boundary conditions at the contact area. As well, a form of hysteresis in the relationship between terminal solid solubility and temperature is included in the model in order to be able to predict some of the phenomenon observed during controlled laboratory experiments.

The formulation and coding have been added to an existing in-house structural analysis computer program [1] which has become an important tool in the investigation of CANDU pressure tube structural integrity.

### 1. Introduction

The CANDU Zircaloy-2 pressure tube failure in Pickering 'A' Unit 2, in August 1983 during reactor operation, resulted from the propagation of a crack which initiated at solid zirconium hydride concentrations (or blisters) on the outer surface of the pressure tube where it contacted the much cooler surrounding calandria tube. The pressure tube had picked up sufficient hydrogen (in the form of deuterium) during operation that subcritical crack growth, by delayed hydride cracking, could have occurred at operating temperature. In addition, many of the precipitated hydrides within the tube were in the radial-axial orientation thereby reducing the fracture toughness for axial crack propagation.

The complete explanation of the failure requires an understanding of the pressure tube/calandria tube contact, the redistribution of pressure tube temperature, the hydrogen migration, precipitation and hydride blister formation and the change in material

<sup>1</sup>hydrogen includes both isotopes <sup>1</sup>H and <sup>2</sup>H which are present in pressure tubes.

properties such as constitutive parameters, material toughness and thermal conductivity during the blister growth. As well, one must determine the effect of blister growth on the pressure tube/calandria tube contact geometry, the stresses developed locally and then investigate the initiation and propagation of cracks under these conditions.

The present study is concerned with the temperature redistribution due to pressure tube/calandria tube contact and the hydrogen migration resulting in the growth of blisters. In the past, simple one dimensional models have been used to make estimates of blister growth rates and other phenomena. Also, the single-phase and the two-phase regions were treated separately with different governing equations for each zone. The difficulty with that approach was that the boundary between the two regions had to be determined as part of the solution. The approach used in the present study is based on the fact that the fundamental governing equations can be re-formulated so that a single set of equations can be used throughout the whole region [2,3].

## 2. The Controlling Equations

The physics of hydrogen migration has been studied extensively [4,5,6,7,8] and the governing equations are well documented. The hydrogen flux, in solution, is given by:

$$\dot{J}_s = -\dot{D}_s \cdot [C_s \dot{\nabla}(\ln C_s) + \frac{C_s Q^*}{RT^2} \dot{\nabla}T] \quad (2.1)$$

and the equation of continuity is

$$\frac{\partial C}{\partial t} = -\dot{\nabla} \cdot \dot{J} \quad (2.2)$$

$\dot{J}$   $\equiv$  total hydrogen flux

$\dot{J}_s$   $\equiv$  hydrogen flux in solution

$C$   $\equiv$  total hydrogen concentration

$C_s$   $\equiv$  concentration of hydrogen in solution

$R$   $\equiv$  gas constant

$t$   $\equiv$  time

$T$   $\equiv$  absolute temperature

$Q^*$   $\equiv$  heat of transport

$\dot{D}$   $\equiv$  diffusion coefficient

The diffusion coefficient is related to temperature through the relationship

$$\dot{D} = \dot{D}_0 e^{-Q/RT} \quad (2.3)$$

where

$Q$  = activation energy for diffusion

$\dot{D}_0$  = frequency factor

and

$$\dot{\vec{D}} = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{bmatrix} \quad (2.4)$$

The general controlling equation

$$\frac{\partial C}{\partial t} = \dot{V} \cdot v_s \dot{\vec{D}} \cdot \left[ \dot{V} C_s + \frac{C_s Q^*}{RT^2} \dot{V} T \right] \quad (2.5)$$

where  $v_s$ , the volume fraction of solution, is obtained by combining equations (2.1) and (2.2) and neglecting the hydrogen diffusion in the precipitate in comparison with that in the solid solution phase. It can be seen that the driving forces for hydrogen diffusion are temperature and hydrogen concentration in solution. (The effect of stress is not included in the model.)

Define normalized concentrations  $S$  and  $S_1$  by

$$S \equiv \left[ \frac{C}{e^{Q^*/RT}} \right] \quad (2.6)$$

and

$$S_1 \equiv \left[ \frac{C_s}{e^{Q^*/RT}} \right] \quad (2.7)$$

The controlling differential equation then becomes

$$e^{Q^*/RT} \frac{\partial S}{\partial t} = \sum_{i=1}^3 \frac{\partial}{\partial x_i} \left[ v_s D_i e^{Q^*/RT} \frac{\partial S_1}{\partial x_i} \right] \quad (2.8)$$

subject to the flux being specified everywhere on the external surface, where

$$(J)_i = -v_s D_i e^{Q^*/RT} \frac{\partial S_1}{\partial x_i} \quad (2.9)$$

The above normalizing factors were chosen since the steady state hydrogen concentration distribution is given by

$$C_s = A e^{Q^*/RT} \quad (2.10)$$

The temperature field is given by

$$\frac{\partial T}{\partial t} = \nabla \cdot (\alpha \nabla T) \quad (2.11)$$

where

$\alpha$  = thermal diffusivity.

The problem then reduces to solving the coupled equations (2.8) and (2.11) where the concentration in solution is determined from the total concentration  $C$  and the terminal solid solubility (TSS). The simplest model for TSS is the expression

$$TSS = C_T e^{-H/RT} \quad (2.12)$$

where

$C_T \equiv$  a constant

$H \equiv$  heat of mixing

The concentration in solution  $C_s$  is the minimum of TSS and  $C$ .

Fortunately, the ratio of thermal diffusivity to the hydrogen diffusion coefficient is in the order of 100 000. Therefore, after some disturbance, the temperature field reaches a new steady state almost instantaneously in comparison to the diffusion of hydrogen. The solution procedure then is to solve equation (2.11) for the steady state temperature in the pressure tube due to a prescribed pressure tube/calandria tube contact. Then knowing the initial hydrogen concentration and the temperature distribution, equation (2.8) is solved as a function of time. This equation holds for both the single phase and two phase regions with the stipulation that

$$C_s = C \quad \text{single phase}$$

$$C_s = TSS \quad \text{two phase.}$$

Also, since the hydrogen concentration in a hydride precipitate is assumed to be 16 000 ppm, the maximum concentration at any point is 16 000 ppm and when this occurs, the solution volume fraction becomes zero and equation (2.8) becomes

$$\frac{\partial S}{\partial t} = 0$$

The temperature field must be updated from time to time as the blister grows.

### 3. Numerical Solution

The capability for the heat conduction part of the solution exists in the form of an in-house finite element code [1]. Separate studies are on-going to determine the best values for the thermal boundary conditions, particularly at and near the contact area.

Modelling of the hydrogen diffusion and blister growth has been carried out using both the finite difference and the finite element method. The finite difference equations were derived by balancing fluxes at the boundaries of cells surrounding each node. These models were useful for parametric studies, and to prove out the basic analytical model through comparison of analytical results with those of carefully-controlled laboratory experiments. The equations for the finite element formulation were derived using the Petrov-Galerkin method, except for the two phase region where the equations could be obtained directly since the concentration in solution is known everywhere in this region. The coefficient matrix is symmetric everywhere except for elements on the two phase/single phase boundary. Therefore, a non-symmetric solver is used. Also, brick elements are used since both the pressure tube and calandria tube have uniform regular geometry. The combination of heat conduction and hydrogen diffusion capabilities provides a powerful tool for studying the blister growth dynamics under various conditions.

#### 4. Improvements in the Modelling of TSS

Although the model, as described above, works very well and predicts results that compare well with laboratory and field inspection results, the model was not capable of predicting certain phenomena that are known to occur. These are:

- a) It is possible to have zero hydrogen flux in a finite thermal gradient with an unlimited supply of hydrogen in the form of hydride.
- b) Blisters may have a maximum size even when the bulk hydrogen concentration is larger than TSS.
- c) For a given hydrogen concentration, hydride precipitation occurs at a lower temperature than hydride dissolution.
- d) During corrosion, under isothermal conditions, zirconium alloys may absorb hydrogen to the extent that TSS is exceeded in the bulk of the material.

When TSS is a single-valued function of temperature as given by equation (2.12), the model is unable to predict the above phenomena. An improvement was achieved by specifying one TSS for precipitation (TSSP) and another for dissolution (TSSD). These curves are shown in Fig. 1 for data generated for Zircaloy-2 [9]. Concentration in solution cannot be larger than TSSP. Therefore, extra available hydrogen must take the form of precipitate. Also, the concentration in solution cannot decrease below TSSD without first dissolving all of the available precipitate at that point. This modification to the model results in the first 3 of the above 4 anomalies being resolved.

A further improvement to the model is based on a suggestion by Marino [10] whereby the rate of increase in precipitate is proportional to  $(C_g - TSS)$ . Our current model stipulates that the rate of increase of precipitate is proportional to  $(C_g - TSSP)$  for  $C_g > TSSP$  and the rate of dissolution of precipitate is proportional to  $(TSSD - C_g)$  for

$C_g < TSSD$  when there is precipitate present. This modification results in the model being able to predict the phenomenon described in (d) above.

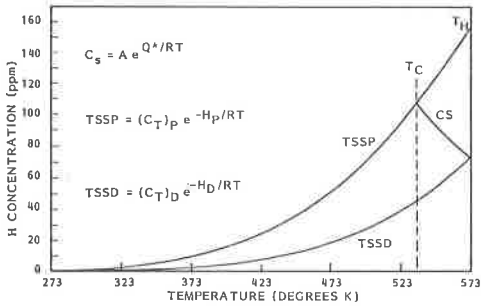


FIGURE 1  
STEADY STATE HYDROGEN DISTRIBUTION

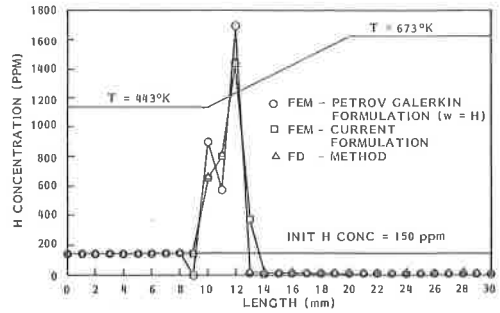


FIGURE 2  
HYDROGEN DISTRIBUTION IN Zr-2.5% Nb  
AFTER 50 DAYS

## 5. Results

The improvements in the modelling of TSS have enabled the current model to predict certain phenomena. For example consider a linear temperature drop from  $T_H$  to  $T_C$  over the length of a specimen. Assume that there is a hydride layer at the hot end ( $T_H$ ) of the specimen. The current model predicts that for temperature drops ( $T_H - T_C$ ) less than that shown in Fig. 1, a steady state hydrogen distribution develops such that the flux becomes zero before precipitation can occur at the cold end of the specimen.

Figure 2 shows a comparison of the predicted hydrogen redistribution in Zr-2.5%Nb, after 50 days, due to the prescribed stepwise linear temperature distribution. It can be seen that the results of the current finite element formulation, compare very well with the finite difference (finite volume) approach. However, the results obtained using the Petrov-Galerkin formulation (with the weighting function equal to the shape function) have "wiggles" in the two-phase region. Although it is possible to correct these problems for 1-D problems by redefining the weighting functions as prescribed in the literature, there is a reasonable amount of uncertainty in being able to correct these problems for all 3D applications. Therefore, the formulation as described in Section 3, is being used with good success.

## References

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