HYDRIDE INDUCED EMBRITTLEMENT OF ZIRCONIUM ALLOY PRESSURE TUBES

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ABSTRACT

Tubes made of dilute Zirconium alloys, act as miniature pressure vessels in Pressurized Heavy Water Reactors (PHWRs) and are subjected to aqueous corrosion, resulting in hydrogen pick up. Hydrogen exceeding solid solubility, precipitates out as brittle hydride phase and may cause embrittlement of the host matrix. Two forms of hydride embrittlement have been recognized for dilute zirconium alloys – gross and localized. Gross embrittlement is caused due to uniformly distributed hydride precipitate, whereas localized embrittlement is caused by hydrogen migration, leading to damage accumulation within a small region over a period of time, before catastrophic failure of the component may occur. Parameters like fracture toughness, threshold stress for reorientation of hydrides, threshold hydrogen concentration for blister formation, Delayed Hydride Cracking (DHC) velocity, threshold stress intensity factor for DHC initiation, are used as fitness for service assessment of pressure tubes. In this article, some of the results generated by Materials Group, BARC, using Indian pressure tube material are highlighted.

Introduction

About ninety water-cooled nuclear reactors in the world, which are either in operation or are under construction, use pressure tubes instead of pressure vessels, to contain the hot pressurized coolant. These reactors are cooled and moderated by heavy water and hence are known as Pressurized Heavy Water Reactors (PHWRs) [1]. Each coolant channel assembly of PHWRs, comprises of a Pressure Tube (PT), a Calandria Tube (CT) and garter springs. Natural uranium oxide powder compacted and sintered in the form of pellets and encapsulated in thin cladding, forms the fuel pins of the PHWRs. Several such pins are assembled in the form of fuel bundles and are loaded in horizontal pressure tubes. Pressure tubes act as miniature pressure vessels in PHWRs, with coolant heavy water flowing through it under a pressure of around 10 MPa and at a temperature in the range of 523 to 573 K and are exposed to a fast neutron flux of $3 \times 10^{17}$ n/m$^2$/s. Calandria tubes surround the pressure tubes from outside. Garter springs are provided at regular intervals in the annular space, to support pressure tube and to prevent it from contacting the cooler calandria tube, which is surrounded by low-pressure, low-temperature heavy water moderator, maintained at 333 K, in a large stainless steel vessel called calandria vessel.

The use of natural UO$_2$ as fuel in PHWRs demands that core structural materials such as cladding tubes (also called fuel tubes), pressure tubes (coolant tubes),
calandria tubes and garter springs must have low neutron absorption cross-section and should satisfy the physical, mechanical, metallurgical and chemical requirements of radiation environment [2]. Pressure tubes being the final pressure boundary containment for hot coolant in PHWRs, their integrity is to be maintained during reactor operation. Though the specification limit for hydrogen content in the pressure tubes is 5 ppm for quadruple melted and 25 ppm by weight for double melted Zr-2.5Nb pressure tubes, part of the hydrogen / deuterium evolved during service from coolant-metal corrosion reaction, is picked up by the pressure tubes. Hydrogen present in excess of solid solubility precipitates out as hydride phase, which is known to embrittle the host matrix. The hydrogen-related problems associated with Zr-alloy components are hydride embrittlement [3] especially due to stress-reorientation of hydride, Delayed Hydride Cracking (DHC) and hydride blister formation. Considering the technological importance of hydride embrittlement of Zr-alloy in safety assessment and life management of Zr-alloy core components. The Materials Group, BARC is pursuing a comprehensive study on hydrogen / hydride induced degradation mechanisms associated with Zr-alloys, involving extensive experimentation and theoretical computations. This article highlights some of the major achievements in this area.

The pace of research and development work in this area, is controlled by hydrogen charging in Zr-alloy samples, without altering its microstructure and texture under laboratory conditions. Thus the primary focus was on the development of a reliable hydrogen charging system. Both gaseous and electrolytic hydrogen techniques are being regularly used by us and are described briefly in section 2 [4]. For fracture toughness and DHC tests, direct current potential drop system was developed in-house, to measure crack length, the salient features of which are described in [5].

The maximum amount of hydrogen which can be retained in solid solution without forming hydride precipitate is called Terminal Solid Solubility (TSS). TSS of hydrogen in zirconium alloys, is observed to increase with increase in temperature. At ambient temperature, TSS of hydrogen in zirconium alloys, is less than 1μg/g. Hence, at ambient temperature almost all the hydrogen in zirconium alloy will be present as hydride. Initially, TSS was thought to be a safe limit for hydrogen concentration, below which embrittlement effect was not considered significant. However, recent studies have shown, that the threshold hydrogen concentration for DHC initiation and hydride blister nucleation are not TSS but a fraction of TSS. Thus, terminal solid solubility of hydrogen in these alloys, is an important parameter and is used by design and safety engineers, for fitness for service assessment of these components. Experimentally TSS is determined by preparing samples with known concentration of hydrogen and measuring some change in physical property, to identify transition temperature. Techniques like dilatometry [6,7], resistivity [8], internal friction [9-11], differential scanning calorimetry [12], small angle neutron scattering [13-14] and metallography [15] measure changes in dimension, resistance, damping frequency, heat flow, lattice parameter and microstructural features, respectively and are used to determine the transition temperature. The experimentally determined transition temperature is correlated with hydrogen concentration, in the form of an Arrhenius-type relationship, to obtain the pre-exponential constant and the enthalpy of the dissolution or precipitation process. With the help of these constants, TSS at any temperature can be obtained. Also, for a sample of unknown hydrogen concentration by determining the transition temperature corresponding to heating and / or cooling total hydrogen content of the sample can be estimated, using the aforementioned constant. TSS values determined for zircaloy-2 and Zr-2.5Nb alloy using dilatometry is presented in [16-17].

Hydride being brittle, makes the host matrix susceptible to embrittlement. Two forms of hydride embrittlement have been recognized for hydride forming metals - gross and localized [3]. The former requires certain minimum volume fraction of the hydride phase and results in overall reduction in tensile
ductility, impact and fracture toughness. Since hydride embrittlement is a major life limiting factor for the components made from these alloys, several theoretical and experimental studies have been carried out, to understand the influence of hydrogen/ hydride on the mechanical properties in general and micromechanisms assisting crack nucleation and its propagation in the presence of hydride, in particular [18]. The influence of hydrides on fracture toughness parameters of Zr-2.5Nb pressure tube material is brought out in [18].

The Zr-2.5Nb alloy pressure tubes for the Indian PHWRs are manufactured at the Nuclear Fuel Complex (NFC), Hyderabad, following a fabrication route similar to the modified route II developed by the Atomic Energy of Canada Limited (AECL) for the Pressure Tubes (PT) of CANDU reactors. The modified route II consists of two cold working steps (instead of one cold working step in the conventional route) and an intermediate annealing step. The lower extrusion ratio employed in the modified route as compared to the conventional route, ensures lower aspect ratio of grains, less intense circumferential basal pole texture and more uniform microstructure, resulting in improved irradiation resistance, reduced susceptibility to stress reorientation of hydrides, and uniform mechanical properties across the length of the tube [19]. Two minor differences in the fabrication steps of Indian tubes and modified route II developed by AECL need to be noted: viz., (i) the amount of cold work imparted during first cold working stage of tube fabrication at NFC is larger (50-55%) as compared to the modified route II (20%) followed by AECL and (ii) compared to cold drawing practiced by AECL, at NFC, cold work is imparted using a process called pilgering, which imparts simultaneous reduction of wall thickness and diameter.

During fabrication of Cold Worked and Stress-Relieved (CWSR) Zr-2.5Nb pressure tube, majority of the α-Zr grains acquire an orientation with their basal poles, oriented predominantly along the circumferential (~55%) and radial (~43%) direction [19]. Since hydride precipitation in a-α-Zr grains show a habit plane nearly parallel to basal plane [20-21], for the texture of the pressure tube material, crystallographically only two orientations are permissible. These are along the circumferential-axial plane and along the radial-axial plane. Hydride platelets oriented along the circumferential-axial plane are called circumferential hydrides and those oriented along radial-axial plane are called radial hydrides [22]. Under unstressed condition, only circumferential hydrides form in Zr-2.5Nb pressure tubes. However, due to stress reorientation phenomenon, radial hydrides may precipitate and being oriented normal to hoop stress direction of the pressure tubes, can significantly increase the latter’s susceptibility to failure. The phenomenon of precipitation of radial hydrides, when cooled under stress from solution annealing temperature, is known as stress-reorientation of hydrides. For dilute Zr-alloy pressure tubes, this translates to precipitation of radial hydrides under hoop stress, as compared to the precipitation of circumferential hydrides in the unstressed condition. This is usually associated with a critical stress called threshold stress below which, no reorientation occurs. The stress reorientation behaviour for Zr-2.5Nb alloy is presented in [23-25].

Delayed Hydride Cracking (DHC) [22] is a form of localized hydride-embrittlement phenomenon, which in the presence of a hydrostatic stress-field manifests itself as a sub-critical crack growth process. It is caused due to hydrogen migration up the hydrostatic stress gradient to the region of stress concentration. Once the local solid solubility is exceeded, brittle hydride nucleates normal to tensile stress. Growth of hydride nuclei continues till hydride platelet of a critical size is formed. Hydride platelet of the critical size cracks under concentrated stress, leading to the growth of the crack. This crack growth is delayed by the time required for hydrogen to reach the crack tip and form hydride platelet(s) of critical size. Hence this phenomenon is called Delayed Hydride Cracking. DHC behaviour of this material is described in section 7 [26-34] in terms of DHC velocity, activation energy and threshold stress intensity factor.
In PHWRs, Calandria Tube (CT) surrounds the PT concentrically from outside and separates the cool moderator (at $-343$ K) from hot coolant (at 523-563 K). Though, Garter springs are provided at regular intervals in the annulus gap between the PT and CT, to prevent PT-CT contact, either due to garter spring displacement from the designed location or due to creep or both, the PT sags and may contact CT, resulting in setting-up of thermal gradient in the PT. Hydrogen migration under thermal gradient in zirconium alloys results in formation of hydride blisters. An array of blisters makes Zirconium alloy components of nuclear reactors susceptible to fracture. The whole process of hydride blister formation and fracture of these components is very complex and involves hydrogen migration under thermal gradient, hydride precipitation, trapping of the matrix, setting up of hydrostatic stress gradient, enhanced hydrogen migration under the combined influence of thermal stress gradient, stress-reorientation of hydrides, cracking of hydrides, crack growth by delayed hydride cracking mechanism, interlinking of blisters and spontaneous fracture of the component. The stress components in hydride blisters and the surrounding matrix for certain assumed blister depths were determined for semi-ellipsoidal blister using Finite Element Method (FEM) and are described in [35-39].

Hydride acquires plate shaped morphology and the broad face of the hydride plate coincides with certain crystallographic plane of $\alpha$-Zr crystal which is called habit plane. Two different theoretical approaches are used, to determine the shape and habit plane of precipitates viz., geometrical and solid mechanics [40]. For the geometrical approach, invariant plane and invariant-line criteria have been applied successfully and for the solid mechanics approach, strain energy minimization criteria have been used successfully [41-43]. Even though the aforementioned theoretical approaches are different, they often predict same shape and orientation for plate type inclusions [44]. Solid mechanics approach using strain energy computed by FEM technique have been applied to hydride precipitation in Zr-alloys, but the emphasis has been on understanding the solvus hysteresis [45-47]. A FEM based technique used to predict the habit plane of $\delta$-hydride precipitating in $\alpha$-Zr using strain energy minimization technique, is described in [48-49].

Hydrogen charging techniques [3-4]

Gaseous hydrogen charging and electrolytic hydrogen charging techniques are widely used, for introducing controlled amount of hydrogen in Zr-alloy samples. In gaseous hydrogen charging technique, Zr-alloy samples are heated in hydrogen atmosphere, either under constant pressure for different time-periods or in a constant volume system. In the former i.e. constant hydrogen partial pressure system, time-period for which the sample is exposed, determines the hydrogen concentration. In the constant volume system, the average hydrogen concentration of the sample is estimated from the product of system volume and the difference between the initial and final partial hydrogen pressures of the system. The beauty of this technique is that, the samples can be hydrieded completely i.e. the amount of hydrogen charged is not limited to the terminal solid solubility of hydrogen in the alloy. Further, this technique can also be used for charging hydrogen under constant pressure. Fig. 1(a) shows photograph of gaseous hydrogen charging apparatus.

In electrolytic hydrogen charging technique, first sufficiently thick and adherent layer of hydride is deposited on the sample surface. The sample with hydride layer is homogenized at a pre-determined temperature, to attain equilibrium. After homogenization, the excess hydride layer is removed by machining. In this technique, the amount of hydrogen charged into the sample, cannot exceed the TSS at the homogenization temperature.

Direct Current Potential Drop (DCPD) technique [5]

The electrical potential drop method is one of the most commonly used techniques, for measuring crack initiation and crack growth, at elevated temperatures. In this technique, the increase in electrical resistivity
of a specimen to which a constant DC current is applied is used, to monitor crack extension. The main advantages of the dc potential drop method are the comparatively simple test set-ups and the capability of the technique to derive a correlation between crack length and potential drop in a certain type of specimen, by means of either analytical or numerical calculations. By measuring DCPD output across standard specimens with known crack length and by plotting the normalized DCPD output against the crack length (a) or the normalized crack length, a/W (where W is the specimen width), a calibration curve can be generated. Similarly, by measuring the DCPD output as a function of temperature, the temperature dependence of the output voltage can be established. A combination of these two curves can be used, for crack growth monitoring. The main features of the DCPD system used for crack growth monitoring are described below.

DCPD system consists of a constant current unit to supply a constant dc current, an arrangement to supply this current through specimen, an arrangement to measure the potential drop across the notch/crack in the specimen and provision to record the DCPD output, temperature and current continuously. The current was supplied to the specimen through screw tightened copper lugs, welded to copper wires. The DCPD output was measured using the wire of the same material (in this case Zr–2.5Nb), to avoid error due to thermocouple effect. For this purpose, 0.5 mm diameter Zr–2.5Nb wires were spot-welded to CCT specimen, within 1 mm of each side of the notch. A constant dc current was used for fracture toughness and DHC tests. The DCPD signal, specimen and furnace temperatures and current were continuously recorded on 12-channel videographic XY recorder. This DCPD system has been developed by the Materials Group,
using in-house resources and expertise and is being regularly used for crack length estimation, during fracture toughness and DHC tests.

**Terminal Solid Solubility (TSS) [16-17]**

When a Zr-alloy sample containing hydride is heated, with increase in temperature, TSS increases resulting in dissolution of hydride in the matrix. For zirconium alloys, hydride dissolution is associated with increase in sample volume. On the other hand, when zirconium alloy sample containing hydrogen is cooled down, hydride precipitation takes place, resulting in decrease in sample volume. Using dilatometer, it is possible to detect the temperature corresponding to end of hydride dissolution during heating and beginning of hydride precipitation during cooling. For a given hydrogen concentration, the temperature corresponding to end of dissolution is called $T_{TSSD}$ and the temperature corresponding to beginning of precipitation is called $T_{TSSP}$. On the other hand, for a given temperature, the amount of hydrogen in solution during heating and cooling are called $T_{TSSD}$ and $T_{TSSP}$, respectively.

Both $T_{TSSD}$ and $T_{TSSP}$ for hydrogen in zircaloy-2 and Zr-2.5Nb pressure tube material was determined, using dilatometry from thermal strain ($e$) vs. $T$ plots, its average slope ($m$) vs $T$ plots and differential strain (Diff. $e$) vs $T$ plots. The average slope was the ratio of change in length of the sample and temperature with respect to reference values. The differential strain was taken as the difference between the strains of the hydrogen charged sample and that of the unhydried one. The values of the Arrhenius parameters i.e. pre-exponential constant, $A$, and heat of solution, $\Delta H_\ell$, for zircaloy-2 and Zr-2.5Nb pressure tube material are listed in Table 1. As is evident from this table, the values of TSSD and TSSP, obtained by the three methods were in good agreement. Though very small scatter was observed between the TSSD values obtained in the present investigation, the TSSP values obtained from the three methods were nearly identical.

Once solid solubility is exceeded hydride phase precipitates in Zr-alloys. A typical micrograph revealing hydrides in Zr-2.5Nb pressure tube material, is shown in Fig. 2(a). For a given hydrogen content, two features of the traces of hydride on Radial-Circumferential (RC) plane and that on the Axial-Radial (AR) plane of the pressure tube, are to be noted in this figure. Firstly, the trace on radial-axial plane is straighter and longer as compared to the trace on radial-circumferential plane. This is expected because the longer $\alpha$ phase grain dimension along the axial direction of the pressure tube, provides uninterrupted growth along axial direction. The branching of the hydride on the

**Table 1: The pre-exponential constant $A$ and Enthalpy of the hydride dissolution or precipitation obtained during heating and cooling for zircaloy-2 and Zr-2.5Nb (in parentheses) pressure tube materials [16-17].**

<table>
<thead>
<tr>
<th>Transition temperature obtained from</th>
<th>$\Delta H_\ell$ (kJ/mol)</th>
<th>$A$ (kcal/mol)</th>
<th>Regression coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Heat up cycle</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strain vs. temperature</td>
<td>30.003 (35.44)</td>
<td>38177.7 (63576.55)</td>
<td>0.9352 (0.95)</td>
</tr>
<tr>
<td>$m$ vs. temperature</td>
<td>33.78</td>
<td>81626.0</td>
<td>0.9554</td>
</tr>
<tr>
<td>Differential Strain vs Temp.</td>
<td>34.55</td>
<td>94041.5</td>
<td>0.9192</td>
</tr>
<tr>
<td><strong>Cool down cycle</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strain vs. temperature</td>
<td>25.93 (17.21)</td>
<td>28536.5 (3235.6)</td>
<td>0.9626 (0.96)</td>
</tr>
<tr>
<td>$m$ vs. temperature</td>
<td>26.00 (17.99)</td>
<td>29250.0 (3789.5)</td>
<td>0.9573 (0.94)</td>
</tr>
<tr>
<td>Differential Strain vs Temp.</td>
<td>26.315 (22.82)</td>
<td>31236.0 (12209.8)</td>
<td>0.9663 (0.99)</td>
</tr>
</tbody>
</table>
radial-circumferential plane, is due to shorter grain dimension along the circumferential direction of the pressure tube. Interesting microscopic details of the circumferential hydride plates are brought out in Fig. 2(b). The hydride plates, which appear as a single entity under optical microscope, show two sub-microscopic levels of organization. At platelet level of organization, the hydride plates comprise of several smaller hydride platelets, stacked with a near parallel orientation with respect to each other. At sub-platelet level of organization, each hydride platelet was observed to be comprising of several tiny sub-platelets, stacked closely, either laterally or end to end.

Fracture Toughness [18]

The material used for fracture toughness tests were from double melted, autoclaved, unirradiated Zr-2.5Nb pressure tube spools, gaseously charged with different hydrogen concentrations. Metallographic examination suggested that, hydride plates were oriented along circumferential-axial direction of the tube. Curved Compact Toughness (CCT) specimens of width 17 mm were machined from these spools with crack plane along axial-radial plane to facilitate crack propagation along axial direction of the tube. The fracture toughness testing procedure recommended in ASTM

Fig. 2(a): The microstructural features of traces of hydrides on two orthogonal planes (AR and RC) of Zr-2.5Nb pressure tube alloy charged with 73 (60) ppm of hydrogen. Arrow shows the radial direction and axial or circumferential direction in these micrographs is normal to it.

Fig. 2(b): Internal details of circumferential hydride as observed in secondary electron mode.
The variation in critical crack length for the catastrophic failure of pressure tubes under reactor operating condition with hydrogen content and test temperature, is listed in Table 2. The value of $CCL$ computed from $J$ values by iterative method, in the present investigation, was $> 54$ mm for all the hydrogen concentrations and test temperatures. The $CCL$ value was highest at $423$ K and for lowest level of hydrogen.

Stress-Reorientation of Hydrides [23-25]

The threshold stress for reorientation of hydrides was determined, using a hydrogen charged tapered gage tensile specimen, heating it to a solution annealing temperature, to dissolve all the hydrides, cooling from solution annealing to a reorientation temperature, applying a constant load so as to attain stress variation across the specimen axis, and allowing the specimen to cool under load. After cooling, the specimen is slit axially, examined metallographically for hydride orientation, a montaze is prepared for the entire sample, the boundary between radial and circumferential hydride is marked and local and mean standard E-813 was followed in the present investigation, except for the fact that the crack length was determined using Direct Current Potential Drop (DCPD) technique, which facilitated the use of single specimen technique, for fracture toughness parameter determination.

The Influence of test temperature on (a) $J_{0.15}$ and $J_{1.5}$ and (b) mean $dJ/da$ values of Zr-2.5Nb pressure tube alloy, containing different amounts of hydrogen is shown in Fig. 3. The fracture initiation parameters $J_{0.15}$ appear to be mildly decreasing with increase in test temperature, though for the samples containing 21 wt. ppm of hydrogen, the scatter in data was large. The crack propagation parameters such as $J_{1.5}$ and mean $dJ/da$, increased with increase in test temperature and appear to be reaching a saturation value at higher test temperatures, suggesting that, this data represents the high temperature part or upper shelf of the typical S-curve, exhibited by the temperature dependence of fracture energy. It may be noted that, the mean $dJ/da$ data showed least scatter as compared to other parameters. Also, the difference between crack initiation fracture toughness parameters and crack propagation parameters increases, with increase in test temperature.

The threshold stress for reorientation of hydrides was determined, using a hydrogen charged tapered gage tensile specimen, heating it to a solution annealing temperature, to dissolve all the hydrides, cooling from solution annealing to a reorientation temperature, applying a constant load so as to attain stress variation across the specimen axis, and allowing the specimen to cool under load. After cooling, the specimen is slit axially, examined metallographically for hydride orientation, a montaze is prepared for the entire sample, the boundary between radial and circumferential hydride is marked and local and mean
threshold stresses are determined [23-25]. Leger and Donner [50], based on their observation of the existence of a marked boundary between the radial and circumferential hydrides across the thickness of the pressure tubes, concluded that, a variation in threshold stress across the pressure tube thickness, is due to residual stresses in these materials. The difference between the mean threshold stress value and the local threshold stress across the thickness, yielded the residual stress variation, across the pressure tube thickness.

Fig. 4 shows the variation of the mean threshold stress with reorientation temperature and is observed to decrease with increase in reorientation temperature. The threshold stress for reorientation of hydrides in CWSR Zr-2.5Nb pressure tube material, shown in Fig. 4, were determined using a tapered gage tensile specimen, having its axis parallel to circumferential direction of tube. The tapered gage specimens were gaseously charged with controlled amount of hydrogen and subsequently allowed to cool under a constant load. A montage of the micrographs prepared by sectioning the specimen along its axis, revealed hydride plate orientation as a function of stress. A unique value of the threshold stress called mean threshold stress for reorientation of hydrides in dilute zirconium alloys, was determined by two methods, viz. half thickness methods and area compensation method [50]. Also plotted in Fig. 4 for comparison, is the mean threshold stress value for this alloy, reported by Singh et al [23].

Fig. 5 shows the variation in residual stress (difference of local threshold stress and its mean value) across the thickness of the pressure tube, at various reorientation temperatures. It was observed that the residual stresses are tensile near the inside diameter of the tube, whereas, these are compressive towards the outer diameter of the tube. Both the peak residual tensile and compressive stresses, were observed to decrease, with increase in reorientation temperature [24].

Delayed Hydride Cracking [5,26-34]

DHC is a discontinuous crack growth process and is usually associated with an incubation period to crack initiation, a stable crack growth velocity called DHC velocity ($V_{DHC}$) and a threshold stress intensity factor - SIF ($K_{th}$). Below $K_{th}$, $V_{DHC}$ is negligible and above this threshold $V_{DHC}$ increases rapidly with increase in SIF up to $K_c$ (SIF corresponding to initiation of plastic yielding at the crack tip). For SIF greater than $K_{th}$, $V_{DHC}$ is independent of the SIF. A second higher threshold SIF corresponds to fracture toughness of the material above which, crack grows in an unstable manner. $V_{DHC}$ is influenced to a varying degree by test temperature, direction of approach of test temperature, strength of alloy, hydrogen content, crystallographic texture and microstructure of the material.

Table 2: CCL (mm) for catastrophic failure of Zr-2.5Nb pressure tubes under PHWR operating condition computed from $J_c$ values obtained in this work at various test temperatures and hydrogen contents [18].

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Temperature, K</th>
<th>21 wt. ppm</th>
<th>70 wt. ppm</th>
<th>90 wt. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>306</td>
<td>57.6</td>
<td>56.0</td>
<td>56.0</td>
</tr>
<tr>
<td>2.</td>
<td>373</td>
<td>59.6</td>
<td>54.8</td>
<td>59.2</td>
</tr>
<tr>
<td>3.</td>
<td>423</td>
<td>73.0</td>
<td>55.0</td>
<td>59.2</td>
</tr>
<tr>
<td>4.</td>
<td>473</td>
<td>61.2</td>
<td>60.4</td>
<td>--</td>
</tr>
<tr>
<td>5.</td>
<td>523</td>
<td>65.6</td>
<td>61.8</td>
<td>57.2</td>
</tr>
<tr>
<td>6.</td>
<td>573</td>
<td>57.2</td>
<td>58.0</td>
<td>55.2</td>
</tr>
</tbody>
</table>
Fig. 5: Variation in residual stress across the thickness of the pressure tube at various reorientation temperatures [24].

Fig. 6: The plots of DHC velocity ($V_{DHC}$) in Zr-2.5Nb pressure tube materials with inverse of test temperature [26].

Fig. 7: Plot of DHC velocity with stress intensity factor for unirradiated cold worked and stress-relieved Zr-2.5Nb Indian pressure tube samples tested at various temperatures [27].

Fig. 8 & 9: Stress Field around Hydride Blister [35-39]

For computation of stress field around hydride blister, the matrix of dimension in the ratio 1:5 was considered. Zr was modeled with transversely isotropic elastic constants [51] and zirconium hydride [52] was modeled with isotropic elastic constants. Computations were made corresponding to materials properties at 400 °C for an axisymmetric case, with the symmetry axis along vertical direction (Figs. 8 & 9) and hydride / matrix yield strength ratios of 0.2 and 1.0. The body was partitioned into several small layers, with each layer transformed sequentially (multi-step) or simultaneously (single step). 2263 number of 8-node axisymmetric quadrilateral element
was used. The phase transformation of the zirconium hydrogen solid solution into hydride, was simulated by imposing a temperature rise with appropriate thermal expansion constants to obtain 17.2 % increase in volume or a linear isotropic swelling strain of 5.7%, which was imposed incrementally using ABAQUS FEM package.

The contour plot of the equivalent stress in the blister and matrix around it for the hydride / matrix yield strength ratio equal to 0.2 and computed by multi-step method is shown in Fig. 8. The scale is in units of MPa. It may be noted that the yield stress of the hydride is ~ 60 MPa and that of the zirconium is ~300 MPa [53]. As is evident from this figure, most of the regions inside the blister and matrix, are under negligible stress, with a small strip near the boundary between blister and matrix, under very high stresses. Since the hydride was considered to have lower yield strength as compared to the matrix, most of the volume change is accommodated inside the blister by the plastic flow of hydride.

The contour plot of the equivalent stress inside the blister and the matrix around it, with both the hydride and matrix having identical yield strengths (300 MPa) and computed by multi-step method, is exhibited in Fig. 9. The maximum value of equivalent stress was observed at the interface between blister and matrix. The stress decays as one moves away from the blister matrix interface. All earlier investigators [54-55] have simulated hydride formation by raising the temperature and allowing the phase transformation of the entire hydride in one step. For comparison, the contour plot of the equivalent stress inside the blister and in the matrix around it, computed by single step method, is shown in Fig. 10. As is evident from Figs. 9 & 10, equivalent stresses in the blister and matrix

![Fig. 8: Contour plot of equivalent stress in the soft blister and matrix around it. Phase transformation achieved in multiple steps [38].](image)

![Fig. 9: Contour plot of equivalent stress in the blister and matrix around it for hydride/matrix yield stress ratio equal to unity. Phase transformation achieved in multiple steps [38].](image)

![Fig. 10: Contour plot of equivalent stress in the blister and matrix around it for hydride/matrix yield stress ratio equal to unity. Phase transformation achieved in single step [38].](image)
are higher for a single step transformation, than that for a multi-step transformation. The difference between the hydrostatic stress variation along direction 2 (corresponds to radial direction of tube) computed by single and multiple step methods, are shown in Fig. 11. Since hydride blisters grow sequentially, a single step phase transformation results in overestimation of the equivalent stress.

A section of the hydride blister [36] is shown in Fig.12a. It is evident from this figure, that the section of the hydride blister has three regions. Far away from the center of blister lies region I, comprised of single and multiple step phase transformation results in overestimation of the equivalent stress.

In Fig. 12(b), the threshold stress variation across the sample thickness is superimposed on the plots of computed stress for $\sigma_{11}$ = 0.2, 0.5 and 1.0mm (in the figure it is denoted as $a$ ) [36]. The hydride platelet orientation at any location in the matrix around the blister is governed by the stresses generated due to the hydride blister. For any point in the matrix where prevailing tensile stress is greater than the threshold stress for reorientation of hydrides, radial hydrides will also precipitate out.

**Accommodation Energy of Hydrides and Its Habit Plane (48-49)**

The accommodation energy of $\delta$-hydride in $\alpha$-Zr single crystal was computed by initial strain method. The body was partitioned into two parts viz., Hydride and matrix. Transformation of the zirconium hydrogen solid solution into $\delta$-hydride is associated with about 17 percent positive change in volume [20]. The phase transformation was simulated by imposing a temperature rise in hydride, assigned with appropriate thermal expansion constants. The computation was carried out to determine the influence of hydride plate orientation on the accommodation energy.

The plots of normalized accommodation energy with hydride nuclei orientation for the case where hydride is isotropic elastically and matrix is transversely isotropic elastically, is presented in Fig. 13. The accommodation energy values were normalized with value corresponding to the zero degree orientation, which corresponds to the case where broad face of hydride disk is oriented normal to the c-axis of $\alpha$-Zr hcp crystal. The normalized accommodation energy shows minima for zero degree orientation for fully elastic case, suggesting basal plane of $\alpha$-Zr phase as the habit plane of $\delta$-hydride. However, transformation of $\alpha$-Zr-H solid solution to $\delta$-hydride is associated with about 17 percent increase in volume. Such a large increase in volume is likely to cause plastic deformation of both hydride and the matrix surrounding it. Hence, dependence of accommodation energy on hydride
nuclei orientation, was also determined for elasto-plastic case. The hydride phase was modeled to behave isotropically both elastically and plastically [52]. The matrix phase was modeled to exhibit transverse isotropic elastic behaviour [51] and either isotropic plastic behaviour (plastic or WH) or transverse isotropic plastic behaviour (Hill) [53]. Both perfect plastic

behaviour (plastic) and linearly work-hardening (WH) behaviour was considered. The material model allowed linear increase in flow stress with plastic strain, resulting in ultimate tensile strength 25 percent greater than the Yield Strength (YS) of the material corresponding to a plastic strain of 10 percent.

The plots representing the variation in accommodation energies with hydride nuclei orientation for the elasto-plastic hydride and matrix is shown in Fig. 14. The plots of elastic component of accommodation energies (Fig. 14a), plastic dissipation energy (Fig. 14b) and total accommodation energy (Fig. 14c) with orientation are shown for Iso-YS case, where both hydride and matrix have identical YS. The data in Fig.14 represented by circular symbols, correspond to perfect isotropic plasticity, square symbol correspond to linear work-hardening isotropic plasticity, triangular symbol correspond to perfect Hill’s plasticity and inverted triangular symbol correspond to linear work-hardening Hill’s plasticity behaviour of matrix. Both elastic accommodation and plastic dissipation energy values for linear work-hardening case were always higher than the corresponding values for perfect plastic case, resulting in total accommodation energy values for the former greater than the latter. The elastic accommodation energy values for Hill’s plastic case
was always greater than the corresponding values for isotropic plastic case, whereas plastic dissipation energy for the former was lower than the corresponding values for the latter. However, the difference between the elastic accommodation energy was greater than that for plastic dissipation energy, resulting in total accommodation energy for the Hill’s plastic case being greater than the corresponding value for isotropic plasticity case.

For Iso-YS case (Fig. 14a), the elastic accommodation energy decreases with increase in orientation angle, reaches a minima at 60° and increases marginally with further increase in orientation. The plastic dissipation energy for iso-YS case (Fig. 14b) increased with increase in orientation angle. The plastic dissipation energy dominated the total accommodation energy values, ensuring that, the total accommodation energy increased with increase in orientation angle. Thus for elasto-plastic case also, accommodation energy shows minima for zero degree orientation, suggesting basal plane of α-Zr phase as the habit plane of δ-hydride.

Conclusions

Terminal solid solubility of hydrogen in Zr-alloy was determined using dilatometry and was found to be internally consistent. Up to 90 wppm of total hydrogen content, hydrides plates oriented along the circumferential-axial plane of the tube did not affect the fracture toughness appreciably. The threshold stresses were observed to decrease with increase in reorientation temperature. The difference between the local threshold stress and the mean threshold stress yielded the residual stress, which was observed to decrease with increase in reorientation temperature. For Zr-2.5Nb alloy manufactured by Q&A route delayed hydride crack growth rate ($V_{DHC}$) was lower as compared to those manufactured from CWSR route. Threshold stress intensity factor associated with DHC in unirradiated, cold-worked and stress-relieved Indian Zr-2.5Nb pressure tube alloy, was found to be about 9-11 MPa.m$^{1/2}$ in the temperature range of 476-556K. The stress field in the hydride blister and Zr-matrix were estimated using the finite element method. The computed effective stress obtained by carrying out the single step transformation of a hydride is higher, as compared to that obtained by a multi-step transformation. The stress field could explain the formation of radial hydrides in the matrix near the interface region. For both fully elastic case and elasto-plastic case, the accommodation energy shows minima for zero degree orientation, suggesting basal plane of α-Zr phase as the habit plane of δ-hydride.
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