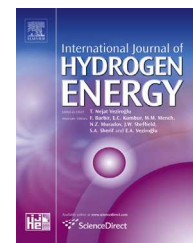


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Review

Hydrogen in Zircaloy: Mechanism and its impacts



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ABSTRACT

Zircaloy is extensively used as a nuclear fuel cladding tube material. The fuel cladding encapsulates radioactive fuel pellet and it is resorted to an exceptionally harsh environment which is the combination of high temperature, high stresses, a chemically aggressive coolant and intense radiation fluxes. Hydrogen or deuterium produced as a result of aqueous corrosion of Zircaloy cladding diffuses into its matrix. Hydrogen diffused into Zircaloy fuel cladding beyond the terminal solid solubility precipitates out as brittle hydride phases. The precipitation of brittle hydride degrades the mechanical properties of Zircaloy so severely that it limits the service life of fuel cladding and may even cause its failure. The failure of Zircaloy cladding due to hydrogen ingress into its matrix is called hydrogen embrittlement or hydride-induced embrittlement. The phenomenon of hydrogen embrittlement is deeply dependent on the behaviour of hydrogen inside the lattice of Zircaloy subjected to the harsh and highly transient conditions of nuclear reactor as a fuel cladding. A plethora of investigations on hydrogen embrittlement has already been reported in the literature. The research investigations pertaining to hydrogen embrittlement are highly scattered with contradictory outcomes. The present article attempts to succinctly summarize relevant research works in order to develop simplistic and coherent understanding of this complex phenomenon, apart from highlighting the thrust areas which require further investigations.

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Introduction

Nuclear power began out of military necessity but since inception this unprecedented power was also seen as having potential to satiate energy thirst. At present nuclear power plants meet over 13 per cent of the world's electricity demand

[1]. Unlike other carbon-less energy resources, nuclear power plants do not disgorge any greenhouse gas and these require less land footprint. Amidst concerns for the climate change propelled by carbon pollution, adoption of policies of carbon release restriction along with exponentially mounting demand for energy; consistent and carbon-free base-load electricity generation is more crucial than ever for the ecosystem.

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Nomenclature

| | |
|--------|---|
| BCC | body centred cubic |
| CNPGAA | cold neutron prompt gamma activation analysis |
| D | deuterium |
| DFT | density functional theory |
| DHC | delayed hydride cracking |
| DNB | departure from nucleate boiling |
| EMAR | electromagnetic acoustic resonance |
| FCC | face centred cubic |
| fct | face centred tetragonal |
| H | hydrogen |
| HCP | hexagonal close-packed |
| HPT | high-pressure torsion |
| IGF | inert gas fusion |
| LOCA | loss of coolant accident |
| PCI | pellet–clad interaction |
| ppm | parts per million |
| RIA | reactivity initiated accident |
| TSS | terminal solid solubility |
| TSSD | terminal solid solubility for dissolution |
| TSSP | terminal solid solubility for precipitation |
| VHE | vacuum hot extraction |
| Zr | zirconium |
| Zr-4 | Zircaloy-4 |

Against this backdrop, steady rise of nuclear energy is imperative in coming years. There are more than 60 nuclear reactors under erection in various countries at present [1]. Nevertheless, safety issues related to nuclear reactors have been a barrier to its wide acceptance and rapid progress. The prime objective of safety measures in nuclear power plants is to prevent failure of fuel cladding as it encases the radioactive fuel undergoing fission. Its failure will not only cause the shutdown of reactor but also pose a potential threat of leakage of radioactive fuel into the environment. Zircaloys, a class of zirconium alloys, are extensively used as a cladding material for nuclear fuel. Zircaloys are preferred to other materials' cladding because of their strikingly low thermal neutron cross-section, apt thermal conductivity, dimensional stability and corrosion resistance in the harsh environment of a reactor core [2]. The chemical compositions of few Zircaloys are provided in Table 1. The search for better mechanical properties and resistance to corrosion of zirconium alloys led to the development of Zircaloy-1 in the nascent stage of

Table 2 – Properties of Zircaloy-4.

| | Alloying element | Weight % |
|---|------------------|-------------------|
| Composition | Tin | 1.20–1.70 |
| | Iron | 0.18–0.24 |
| | Chromium | 0.07–0.13 |
| Properties | Magnitude | Unit |
| Neutron cross-section | 0.22 | Barns |
| Density | 6.55 | g/cm ³ |
| Coefficient of thermal expansion at 25 °C | 6 | μm/m °C |
| Heat capacity | 0.285 | J/g °C |
| Thermal conductivity | 21.5 | W/m °C |
| Melting point | 1850 | °C |
| Modulus of elasticity | 99.3 | GPa |
| Poisson's ratio | 0.37 | – |

nuclear power industry. Tin was introduced to neutralize detrimental effects of nitrogen on corrosion of Zircaloy. The presence of nitrogen was due to the fabrication process used at that time. Later, Zircaloy-1 was replaced by Zircaloy-2 which showed a significant improvement in resistance to corrosion and is still used in boiling water reactors. However, it was observed that the presence of nickel in Zircaloy-2 is responsible for high hydrogen uptake. It made Zircaloy-2 highly susceptible to hydride embrittlement and unfit as fuel cladding of pressurized water reactor which operates at higher temperatures as well as its coolant contains a high concentration of hydrogen. Consequently, the Zircaloy-4 was developed by replacing nickel by iron. Zircaloy-4, whose properties are shown in Table 2, is by far very less vulnerable to hydrogen absorption [3].

Zircaloy fuel cladding may fail due to various reasons, as shown in Fig. 1. Failure of fuel claddings is such a complex phenomenon that it seldom happens because of singular phenomenon rather combination of various phenomena [2]. One of the failure mechanisms associated with Zircaloy cladding is hydrogen embrittlement or hydride-induced embrittlement. This brittle failure occurs due to diffusion of hydrogen and/or deuterium (an isotope of hydrogen) into the Zircaloy cladding. Hydrogen and/or deuterium absorbed by Zircaloy claddings may be produced from any of the following sources [4]:

- Hydrogen and/or deuterium produced during the aqueous corrosion of Zircaloy which takes place at the interface of cladding and coolant (water or heavy water)

Table 1 – Chemical composition of different zirconium alloys.

| Name of alloy | Alloying elements (weight %) | | | | | Utilization |
|---------------|------------------------------|------|----------|--------|---------|------------------------------------|
| | Tin | Iron | Chromium | Nickel | Niobium | |
| Zircaloy-1 | 2.50 | – | – | – | – | Not suitable for reactor operation |
| Zircaloy-2 | 1.50 | 0.12 | 0.10 | 0.05 | – | Boiling water reactor, CANDU |
| Zircaloy-4 | 1.50 | 0.20 | 0.10 | – | – | Pressurized water reactor |
| ZIRLO™ | 1.02 | 0.10 | – | – | 1.01 | Pressurized water reactor |
| M5™ | – | 0.05 | 0.015 | – | 1.00 | Pressurized water reactor |

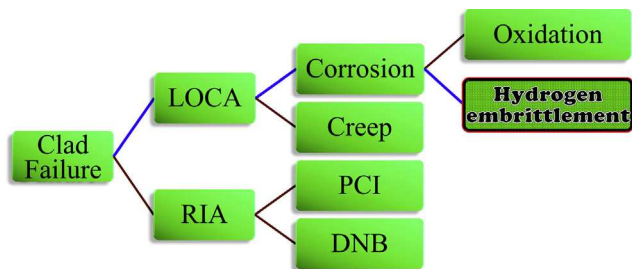
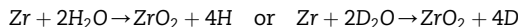
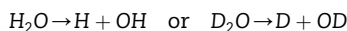


Fig. 1 – Mechanisms of clad failure.

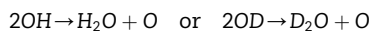


b) Radiolytic decomposition of coolant



c) Presence of moisture in the fuel pellet placed inside cladding

d) Infusion of hydrogen into the coolant for scavenging of nascent oxygen produced during radiolytic decomposition



Diffusion of hydrogen in Zircaloy may severely impact its critical properties like dimensional stability, mechanical strength, its corrosion and creep behaviour etc. The severity of hydrogen ingress or hydride formation in Zircaloy fuel claddings can be assessed from the fact that it is responsible for the determination of service time of fuel claddings. In spite of noteworthy progress in technologies related to nuclear safety, the various phenomena correlated with hydrogen embrittlement remain ambiguous [5]. This review article strives for the development of a better and systematic understanding of the hydrogen embrittlement of Zircaloy-4 fuel cladding by succinctly summarizing the relevant researches reported till the present, with an emphasis on recent outcomes. This understanding may expedite or turn a new leaf in the current research on hydride-induced embrittlement of Zircaloy-4, apart from enlightening the novices in this sphere.

Hydriding mechanism

Zirconium exists as the hexagonal close-packed (HCP) α -phase structure at ambient temperature and pressure as shown in Fig. 2. However, on increasing the pressure to about 2 GPa at the ambient temperature; it transforms into the hexagonal ω -phase. An exact determination of the pressure at which equilibrium transition happens has not been possible due to existence of hysteresis. Experimental investigations have established that hexagonal ω -phase transforms to a body centred cubic (BCC) ω' -phase at a pressure of 35 GPa. Nevertheless, this phase was found to be identical as β -phase. At ambient pressure, zirconium transforms from α -phase to β -

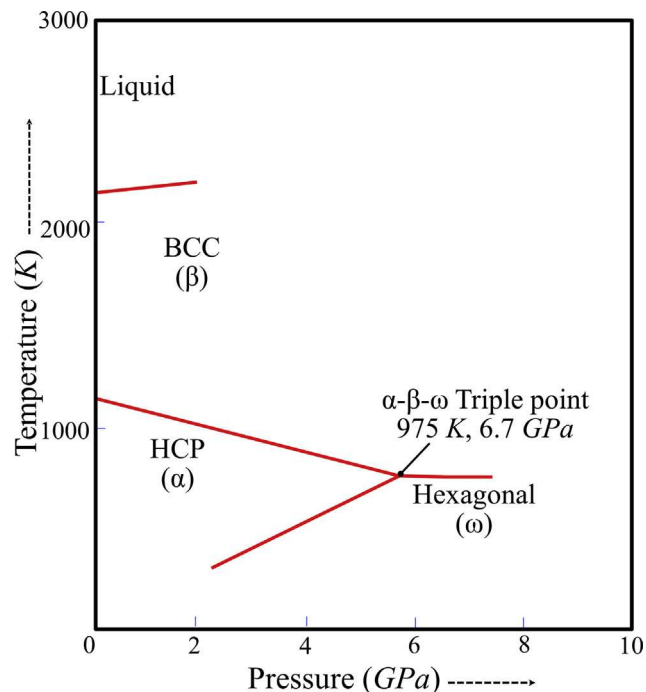


Fig. 2 – Temperature–pressure phase diagram for Zr.

phase at 1139 K. The α – β – ω triple point has been reported to exist at 975 K and 6.7 GPa [4,6].

One of the major sources of hydrogen—picked by Zircaloy fuel claddings—is the aqueous corrosion reaction in which hydrogen is released from the water (coolant) as mentioned in the previous section. In addition to that it is idealistic to avoid formation of a thin oxide layer of 2–5 nm thick even at ambient temperature given large affinity for oxygen of zirconium. This thin oxide layer is observed to be formed in the form of three types of solid solution of oxygen (Zr_2O , ZrO and Zr_2O_3) in the elemental zirconium lattice. These solid solutions of oxygen are called sub-oxides and these three sub-oxides accompanied by the oxide of ZrO_2 are formed on the cladding surfaces in both oxygen and water vapour atmospheres [7–9]. If the oxide layer is continuous, it will act as a protective film as hydrogen has to penetrate into this layer in order to reach the fresh surface of Zircaloy and find a place in its lattice. The presence of O–H bonds in the oxide layer prevents hydrogen diffusion through it [10,11]. However, dissolution of oxide layer is initiated—a) slowly due to parting of hydrogen from the O–H bonds at a temperature of 300 °C, typical temperature of cladding surface during normal operation of a nuclear reactor and b) rapidly due to cracking of O–H bonds to form H_2O and pure oxide around 500 °C, as shown in Fig. 3. The dissolution of oxide layer leads to the formation of micro-cracks in the oxide layer which shorten the path of movement for both oxygen and hydrogen as well as promote a hydrogen rich zone closer to the zirconium surface which acts as ‘hydrogen pump’; thus increasing the weight gain rates and hydrogen uptake by Zircaloy catastrophically [12–15]. This dissolution of oxygen from the oxide layer happens along the grain boundaries of zirconium and that is why it leads to the formation of a number of pores above the metal substrate [16].

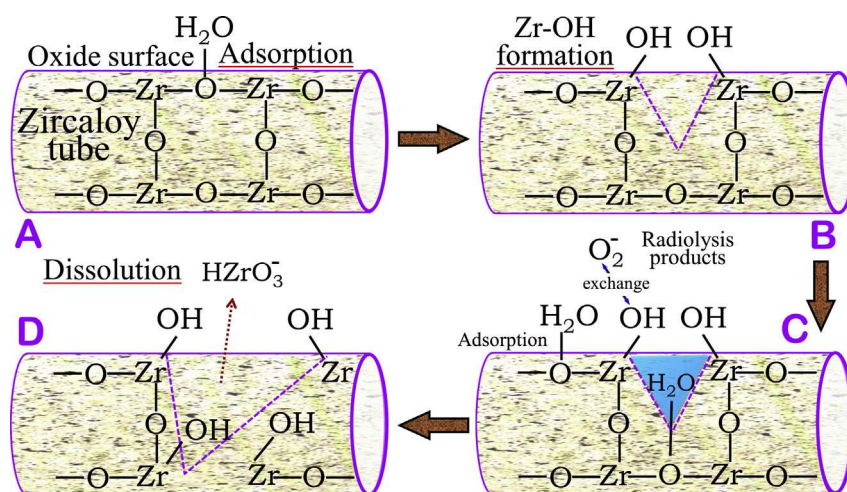


Fig. 3 – Dissolution of zirconium oxide in aqueous medium.

Not all of the hydrogen released during oxidation enters the Zircaloy matrix rather majority of them recombine to form hydrogen gas. There exists a term called hydrogen pickup fraction (f_H) which relates the hydrogen absorbed in the Zircaloy cladding matrix to total hydrogen liberated during corrosion reaction as:

$$f_H = \frac{H_{\text{absorbed in cladding}}}{H_{\text{released in corrosion}}}$$

In spite of the kinetics of hydrogen uptake by cladding being very different than the cladding oxidation kinetics, they have direct interdependence. The hydrogen pickup fraction is functionally dependent upon oxide layer thickness and is found to be non-monotonic in transitional regime. Alloying elements too influence the pickup fraction. Niobium reduces it due to the donor effect while copper increases it for which reasons are not yet resolved. Iron also decreases pickup fraction by lowering potential gradient over the oxide surface required for hydrogen diffusion. Alloys with coarser precipitates exhibit a lower pickup fraction compared to finer precipitates alloys. Hydrogen pickup fraction has also been found to vary with corrosion temperature and exposure time for corrosion; however the mechanisms because of such dependencies exist are not yet clear [17–19].

Although the mechanism of hydrogen invasion through the oxide layer is not agreed universally, different hypotheses have been proposed in order to comprehend the experimental findings. An old but still relevant model, proposed in 1964, argues that diffusion of hydrogen through the oxide layer may be explained by the phenomenon of anion vacancy diffusion [20]. The strong chemical affinity of Zircaloy for oxygen propels the generation of anion vacancies at the interface of fresh Zircaloy and oxide. Oxygen atoms present in the oxide layer migrate to an interstitial location of Zircaloy matrix creating oxygen vacancies. Oxygen ions shift inwards by jumping between anion vacancies, consequently developing a vacancy gradient in the oxide layer and the process continues as shown in Fig. 4 [20]. Nevertheless, later this model was countered on the basis of reasoning that the vacancy created in the oxide layer due to migration of oxygen is too small to

move in comparatively larger hydrogen atom. Hydrogen uptake is then thought to occur through diffusion of hydrogen via the oxide layer along the easy route such as dislocation lines and grain boundaries [21]. Another model, proposed after experimental investigation of hydrogen uptake of Zircalloys in steam environment for the temperature range of 400–600 °C, suggested three possibilities for hydrogen ingress in the Zircaloy matrix through the protective oxide layer. The water molecules react with oxygen vacancies and: (i) hydrogen molecules form after the combination of both protons with electrons present in the vacancies (ii) a proton is removed while OH^- ion diffuses into the oxide film. The proton forms a H_2 molecule together with an electron and a second proton from another water molecule. (iii) OH^- ion moves into the oxide film, while second proton is captured by a negative site on the surface of Zircaloy, then moving to an O^{2-} ion to form a second OH^- ion. The negative site is assumed to be an O^{2-} ion or a site resulting from the presence of foreign cations in the oxide film [22].

Once the amount of diffused hydrogen in the Zircaloy matrix reaches a limiting level at given conditions, the hydride phase is precipitated. The limiting amount of hydrogen that can be diffused in the Zircaloy matrix without the formation of a hydride (secondary) phase is termed as terminal solid solubility (TSS). Precipitation of excess hydrogen (hydrogen diffused beyond terminal solid solubility) as hydride phase depends upon the temperature, hydrogen concentration, cooling rate, alloying elements, and ambient conditions. Experimentally terminal solid solubility demonstrates large hysteresis, as shown in Fig. 5 for Zircaloy-4, between the values obtained during the course of heating and cooling. Terminal solid solubility obtained while heating refers to the end of hydride dissolution and is termed as terminal solid solubility for dissolution (TSSD) whereas terminal solid solubility obtained while cooling refers to the beginning of hydride precipitation and is termed terminal solid solubility for precipitation (TSSP). Since the terminal solid solubility in Zircaloy is less than 1 $\mu\text{g/g}$ at room temperature, entire diffused hydrogen in Zircaloy matrix will be present as hydride even at ambient temperature. The limit of solubility of hydrogen

Figure 1 is a phase diagram of the Zr-H system. The vertical axis represents Temperature in degrees Celsius (°C), ranging from 300 to 950. The horizontal axis represents the H/Zr ratio, ranging from 0 to 2.0. The diagram shows several phase regions and reaction lines. Key features include:

- Zr (α)**: The low-temperature, low-hydrogen phase on the left.
- Zr (β)**: The high-temperature, low-hydrogen phase.
- Zr (α) + δ-Hydride (Cubic)**: A phase region at intermediate temperatures and low to moderate H/Zr ratios.
- Zr (α) + δ-Hydride (Tetragonal)**: A phase region at lower temperatures and moderate H/Zr ratios.
- Hydride (δ → ε)**: The high-hydrogen phase on the right.

 The diagram illustrates the stability of different Zr-H phases as a function of temperature and composition.

phase diagram of Zr–H binary system is updated recently in which γ -phase has been incorporated [34].

The development of hydride phases occurs by simultaneous shifting of zirconium and hydrogen atoms due to shearing i.e. martensitic transformation; however the kinetics for the formation of each hydride phases is significantly different [35]. It is notable that nucleation—an initial process of the crystal formation from a solution, liquid or vapour in which small number of atoms, ions or molecules are arranged in a particular pattern—of hydride precipitates in hexagonal close-packed α -phase zirconium matrix is not homogeneous. The hydrides nucleate on preferred crystal planes in even pure zirconium. In polycrystalline Zircalloys, the grain boundaries are the favourable sites for the hydride nucleation. However, intragranular precipitation is dominant for coarse grain sizes or during rapid quenching [36]. After the calculation of the enthalpies of formation of hydride phases at 0 K, it was revealed that the formation of these hydrides is spontaneous under electrochemical environments of the reactor core [34]. The nucleation of zirconium hydride is steered by the chemical free energy in which the chemical driving force for the precipitation is proportional to the terminal solid solubility [37]. Another study reported that since the formation energies for the all three hydrides are almost equal, their relative stabilities may be influenced by mechanical and thermal contributions to the free energies and hence particular phase nucleation may get modified even by minute variations in their thermo-mechanical treatments [38]. Several experimental investigations have been conducted to determine the thermo-physical properties of zirconium hydride. In the temperature range of 300–700 K, the heat capacity of zirconium hydride is significantly greater than that of pure zirconium and the difference between their heat capacities increases with increase in temperature. The considerable difference in the heat capacities of hydride and pure metal at higher temperatures might have resulted because of contribution of hydrogen to optical mode of lattice vibration of zirconium hydride. The lattice parameters increase slightly with the hydrogen content. Thermal diffusivity decreased with increase in temperature and found not to be influenced by the hydrogen content. The thermal expansion coefficients of the hydrides are greater than that of pure zirconium and it increases with increase in hydrogen amount. The elastic moduli of hydrides are higher compared to that of pure zirconium and found to have direct proportionality with hydrogen content. Young's modulus and yield strength of solid hydrides start to degrade when δ -phase hydride becomes the major phase and these properties attain minima for the ϵ -phase. An abrupt drop in yield strength is observed during change in temperature from room temperature to 150 °C. The micro-hardness of hydride is found to be remarkably higher than that of pure zirconium metal and it decreased with rise in hydrogen content. The hardness of the zirconium hydride increased with decreasing the maximum indentation load [39–42].

Once the amount of hydrogen diffused exceeds the terminal solid solubility limit, hydride precipitates in the Zircaloy matrix. Thus, the exact assessment of hydrogen level in metal matrix is important. Various methodologies employed for the quantification of hydrogen content falls under: destructive and non-destructive techniques. Two destructive techniques,

namely vacuum hot extraction (VHE) and inert gas fusion (IGF) have been widely used. In these destructive techniques, the hydrogen is removed from the sample either by heating it in case of vacuum hot extraction or by melting it in case of inert gas fusion. Subsequently, the hydrogen is collected and measured using a McLeod gauge. These two techniques are well established, fast and economical and above all offer the advantage of a fixed calibration, thus, providing an excellent precision in measurement of hydrogen content. Nonetheless, precision of these techniques is susceptible during the evaluation of low hydrogen content [43,44]. Non-destructive techniques include electromagnetic acoustic resonance (EMAR), neutron transmission techniques, neutron scattering techniques etc. In electromagnetic acoustic resonance method, a stable static magnetic field for an electrically conductive specimen is generated. The variations in resonance frequencies in different directions of samples are quantified as hydrogen content. This method has a limitation of not being able to exactly determine the change in resonance frequencies, either due to oxide formation or presence of alloying elements or hydrides. However, this technique is very popular for in situ measurements [45]. In neutron transmission techniques, a collimated beam of neutron is allowed to strike at the hydrogenated sample and a detector is placed at the back. The detector computes the number of neutrons emerging from the sample without interaction and eventually evaluates the hydrogen amount. This technique is quite useful for detecting even small amount of hydrogen but the total cross section of the hydrogen atom must be known in order to quantify the hydrogen content. Since the total cross section of the hydrogen atom is dependent on its chemical state, it is difficult to find it with precision [46]. As Zircaloy neutron absorption coefficient and incoherent scattering cross-sections are poor, neutron scattering technique is very reliable for the determination of hydrogen content. This technique also provides the information about the phases present in the sample and its sensitivity has been found nearly to 0.4 ppm [47,48]. Recently, two novel non-destructive techniques: cold neutron prompt gamma activation analysis (CNPAA) and laser ultrasound technique (LUT) combined with a simplex-based inversion algorithm are proposed. Cold neutron prompt gamma activation analysis technique is based on quantifying prompt gamma rays after the absorption of cold neutrons in the sample. After that a comparison is made between the rates of detection of characteristic hydrogen gamma rays to that of gamma rays from Zircaloy matrix atoms. The distinctiveness of this method is that it can be utilized for the measurement of hydrogen content variations in a single sample. It can detect as low as 5 weight ppm of hydrogen content. In laser ultrasound technique, collimated acoustic waves are transmitted in the Zircaloy tubes and detected with the use of optical means remotely. Thereafter, inversion algorithm is applied on the measured dispersive wave-speeds in order to characterize the mechanical and geometrical properties such as elastic moduli, wall thickness etc. [49,50].

The core of the reactor where fuel claddings are put in operation is a much complex system. Kinetics of oxidation and hydrogen uptake by Zircaloy fuel cladding is influenced by various parameters. A volume of investigations has been made by researchers worldwide in the past to establish a

universally accepted mechanism for corrosion followed by hydriding of Zircalloys. Significant progress has been made. Nonetheless, there still exist phenomena which need further exploration for the better understanding in order to make Zircaloy safer barrier of radioactive fuel.

Characterization and quantification of hydride

Precipitation of hydride in Zircaloy is an intricate process which is influenced by various parameters such as micro-structure (grain size, texture etc.), thermal history and stress state (applied and residual both) of Zircaloy matrix, hydriding conditions, hydrogen content etc. [51–53]. In an unstressed sample, hydrogen would diffuse into grains of Zircaloy matrix along the certain habit planes—crystallographic planes along which certain phenomenon happens. Various such planes like prism plane of $\{10\bar{1}0\}$, pyramidal plane of $\{10\bar{1}1\}$, basal planes of $\{0001\}$ and $\{10\bar{1}7\}$, twinning planes of $\{10\bar{1}2\}$, $\{11\bar{2}1\}$ and $\{11\bar{2}2\}$ for the diffusion of hydrogen into the hexagonal close-packed structure of Zircaloy matrix are reported in the literature. The reasons for the variation in observance of habit plane are the experimental difficulties in determining the crystallographic relationship between the hydrides and matrix grains, and absence of well-defined process for heat treatments as well as fabrication of cladding. Few of such crystal planes are shown in Fig. 7. Among all these reported habit planes, $\{10\bar{1}7\}$ is the most often observed and schematic

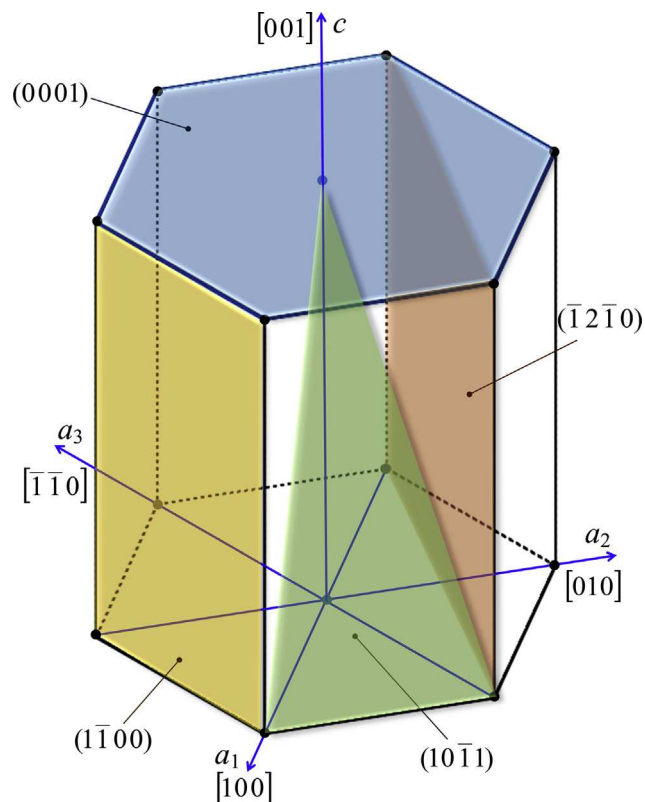


Fig. 7 – Basal $\{0001\}$, Prismatic $\{hk\bar{i}0\}$, and Pyramidal $\{hk\bar{i}1\}$ planes in HCP unit cell.

of hydride orientation on this plane is shown in Fig. 8. On investigations of a cold-worked and unstressed Zircaloy-4 sample charged with hydrogen content in the range of 45–247 weight ppm, it is observed that intergranular hydrides dominate over intragranular hydrides in spite of both following the orientation relationship of $(0001)\alpha - \text{Zr} // (111)\delta - \text{ZrH}_{1.5}$, and this relationship is independent of hydrogen content. The orientation relationship for different hydride phases is provided in Table 4. Grains with higher energy and having its boundaries in proximity to basal plane are preferential site for nucleation of hydride. The strain energy accompanied with the nucleation of intergranular hydrides is influenced by many factors like solute seclusion in grain boundaries, degree of compatibility between hydrides and zirconium matrix, hardening effect of grain boundaries etc. The formation of intergranular hydrides is more uncertain compared to intragranular hydrides and its precipitation can be lessened by reducing grain boundary energy and increasing elastic modulus of the zirconium matrix. Characterization of microstructure of Zircaloy-4 hydride demonstrated long and interlinked hydride chains orientated along the circumferential direction. Tensile twins detected in a sample with lower niobium content are not observed in Zircaloy-4. It is also revealed that the morphology of hydrides is altogether different in weld areas with respect to as-received zone. The hydrides in cold-worked stressed relieved sample are aligned along the rolling direction whereas these are randomly orientated in weld or heat affected zones. Predominantly, a basket-weave Thomson structure or Widmanstatten pattern having a very fine basket-weave α -grain lamellas is present in the weld zone. In this zone, the hydrides are present in form of platelets inside the prior β -grains in which α -grain lamellas have the angular differences of 10° , 60 – 63° and 90° [31,54–63]. Another similar stress-relieved annealed Zircaloy-4 cladding but with higher hydrogen content (300–6000 weight ppm) was analyzed. The δ -phase is precipitated predominantly up to the 1250 ppm; on increasing the hydrogen content to about 3000 ppm, a considerable amount of the γ -phase hydride is also observed [30]. In a different study, γ -phase hydride was also observed at 4000 ppm. The absence of γ -phase hydride at the lower content of hydrogen is probably due to intensity of peak associated with this phase being camouflaged by either background intensity or dominating δ -phase peaks during the measurements. The morphology of hydride and its precipitation with increasing hydrogen content is not similar in stress-relieved annealed and recrystallized Zircalloys. The determination of residual stress does not show any considerable difference between non-hydrided and hydride samples. It is concluded that large, elongated hydrides, and hydrides orientated perpendicular to stress direction crack first in both types of Zircalloys [53]. For stress free field, the grain parameters of the Zircaloy as well as the direction of the previous compressive step in the thermo-mechanical treatment governs hydride precipitation mechanism. The crystallographic texture and the stresses experienced by hydrides precipitated in rolled Zircaloy-4, charged with 200 weight ppm of hydrogen, were investigated. The hydrides precipitated in Zircaloy are detected to be under compressive biaxial stresses of 360 ± 20 MPa in its rolling direction-transverse direction plane. The hydride stresses are strongly influenced

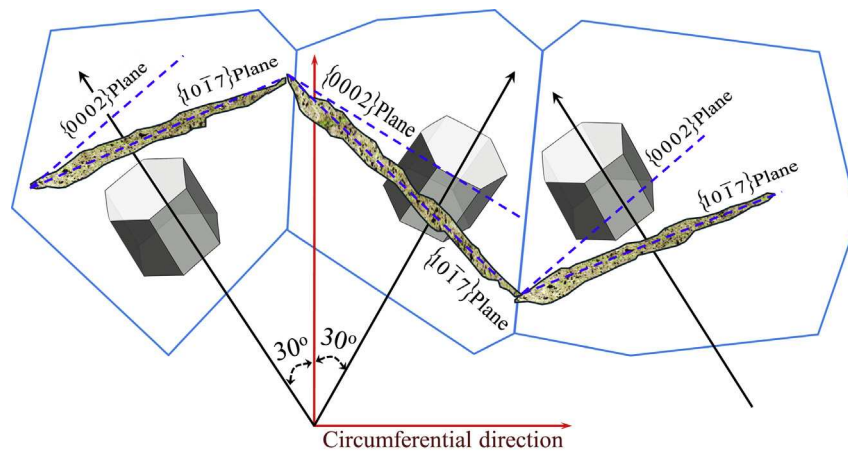


Fig. 8 – Schematic of hydride formation on habit plane $\{10\bar{1}7\}$.

by the grain size of the α -phase zirconium matrix and found to have inverse relation. A large hysteresis was exhibited by hydride stresses, with a steady reduction in the elastic strains on heating and an abrupt change is observed on cooling at the temperature of terminal solid solubility of precipitation [51]. Since the Zircaloy clad tube is subjected to irradiation during its service life, it is critical to understand the microstructural evolution and subsequent deformation of hydride phases caused by irradiation. The δ -phase and ϵ -phase of hydrides were exposed to 6.4 MeV Fe^{3+} ion irradiation in order to simulate the reactor core conditions. For the δ -phase hydrides, the mechanism of deformation consists of both slip and twinning and the hardness of the irradiated sample is about 1.7 times that of unirradiated area. Cracks appeared in both irradiated and unirradiated samples. For the ϵ -phase hydrides, the dominant mechanism of deformation involves both the formation of new fine twin bands and tangled dislocations. A defect of black dot-like structure is also seen in irradiated hydride matrix. The variation in mechanisms of deformation for these two hydride phases may be attributed to difference in their stacking fault energy. It is worth mentioning here that ion irradiation does not change the deformation mechanism in any of these two hydride phases; however, crack formation is more recurrent in the irradiated region of the either phases [64,65]. High-pressure torsion (HPT), one of the severe plastic deformation techniques, which refines the grain size of the metallic sample to nanometer has been used to produce nanostructured Zircaloy-4. This technique improves the strength of Zircaloy-4 and investigations were conducted to find how nanostructured Zircaloy-4 will respond to hydride induced degradation. Large δ -phase hydrides precipitation at 15 atomic ppm incurred considerable hardening of high-pressure torsion samples. Recrystallization texture of α -

zirconium develops from the initial deformation texture while hydriding. High-pressure torsion samples are more prone to hydriding phenomenon in comparison to samples formed under normal crystallization [52,66].

There is no conclusive understanding of hydride precipitation and its actual phase identification and quantification. A number of habit planes for the preferential hydrides precipitation are reported and there is a lack of agreement among these findings, which in turn makes very difficult to propose any fundamental mechanism for establishing the crystallographic correlations between the Zircaloy matrix and hydride phases. There are ambiguities related to parameters for the precipitation of γ -phase hydride and also there is a lack of clear demarcation for its detection. There are major challenges in order to precisely assess the stress evolution in Zircaloy cladding as well as in the precipitated hydride phases during operation of reactor. There is a scarcity of investigation on the microstructural development induced by irradiation as well as the mechanism of deformation under irradiation for Zircaloy-4.

Redistribution and reorientation of hydrides

Since formation of hydrides in Zircaloy is inevitable; it is desirable for internally pressurized tubular components like clad tubes to have circumferentially orientated hydrides as degree of degradation induced by them is less severe comparatively. Fortuitously, the Zircaloy-4 clad tubes have a strong penchant to induct hydrogen in excess of the terminal solid solubility as hydride platelets orientated with their major axis in the circumferential direction. However, usually hydrides are observed to get dissolved at higher temperatures,

Table 4 – Crystallographic relationship for hydride phases.

| Relationship between phases | Crystal orientation relationship | Ref. |
|---|---|------|
| γ -Hydride and α -Zr | $(0\ 0\ 0\ 1)_\alpha // \{1\ 1\ 1\}_\gamma$ and $[11\bar{2}0]_\alpha // [1\bar{1}0]_\gamma$ | [56] |
| δ -Hydride and α -Zr | $(0\ 0\ 0\ 1)_\alpha // \{1\ 1\ 1\}_\delta$, $\{10\bar{1}7\}_\alpha // \{111\}_\delta$ and $[11\bar{2}0]_\alpha // [110]_\gamma$ | [54] |
| γ -Hydride and δ -hydride | $\{1\ 0\ 0\}_\delta // \{1\ 0\ 0\}_\gamma$ | [57] |
| ϵ -Hydride and δ -hydride | $(2\ 2\ 0)_\epsilon // (2\ 2\ 0)_\delta$, $\{111\}_\epsilon // (\bar{1}\bar{1}1)_\delta$ and $\{311\}_\epsilon // (311)_\delta$ | [58] |

and redistribute and reorient themselves—drastically enhancing their degrading capabilities—under the influence of three primary factors: temperature gradient, stress gradient, and the solubility hysteresis during heating and cooling [31,67]. Under operating conditions of fuel clad tubes, there is existence of thermal gradients in axial, radial, and azimuthal directions. In phenomenon involving a heat flux like operation of fuel clad tubes; the increase in heat of solution with decrease in temperature causes the concentration of hydrogen in solution to be little higher in the colder region (usually outer or water side surface of cladding tubes). Thus precipitation of hydride in cladding after redistribution and reorientation is governed, not limited to, by the presence of thermal gradients and it diffuses to colder regions as shown in Fig. 9, in response to different thermal gradients present in claddings. A higher concentration of hydrides is observed in the form of rim like structure called hydride rim at the outer surface of claddings, as there exists a relatively cooler zone due to flow of coolant over it. The average concentration of hydrogen in these hydride rims is 1300 weight ppm while overall concentration in cladding tube is only 430 weight ppm. The coolant temperature increases in vertical or axial direction of the clad tube in the reactor; however, in the regions proximate to spacer grids which are provided for better mixing of coolant, a localized decrease in temperature is observed. This environment of highly transient temperature acts like oxidation and quenching, consequently increasing the concentration of hydrides with height or in vertical-axial direction of fuel claddings. The heat flux produced by the fuel pellet encapsulated by claddings is not uniform throughout; obviously it is higher at the mid-section of pellet than at the inter-pellet gap, giving rise to thermal gradient. Moreover, swelling of fuel pellets, due to which distance between fuel pellet and cladding does not remain symmetrical, is also a cause of fluctuations in heat flux. Hydrides are more localized at the inter-pellet gap which is relatively at slightly lower temperature. Zircaloy clad tubes are used in bundle inside the reactors. It consists as well as interacts with a number of structural components during its operation. These all make heterogeneous in situ environment for clad tubes, creating relatively

lower temperature regions and thus enhancing local hydrides concentration due to which hydride blisters or azimuthal hydrides are formed. Azimuthal hydrides are less reported; however, 400–800 weight ppm of hydrogen in azimuthal region is found for an average cladding concentration of 600 weight ppm of hydrogen. The difference between hydride rims and blisters is that more or less hydride rims cover large area and are distributed uniformly having thickness in range of 50–60 μm whereas blisters are constrained in a narrow zone having elliptical shape and typically penetrate up to half of cladding thickness [68]. The stress gradient too influences redistribution and reorientation of hydrides following the trait of thermal gradient only. With increase in hydrostatic stress in Zircaloy matrix, the concentration of hydrogen increases in the solution; that is hydride will preferably localize in higher stress zone like at the tip of pre-existing cracks. It is worth mentioning here that if both temperature gradient and stress gradient are counterpoised, the temperature gradient will have the pronounced effects. On the fringe, it may appear that thermal cycling should not have any role in redistribution or reorientation of hydrides. However, the existence of hysteresis between dissolution and precipitation as well as presence of unlike neighbouring stress fields for hydrides at different interstitial sites constrains the re-precipitation of hydrides on the pre-existing grain boundaries of hydrides [31].

In order to probe phenomena of hydride redistribution and morphological alterations during high temperature transients (probable during operational occurrences and accidents of fuel cladding), experiments were conducted by rapidly heating hydrided but unirradiated Zircaloy-4 cladding tubes in the temperature range of 400–900 °C and annealed for a holding time in range of 0–3600 s. At the temperature of 400 °C, there is no morphological change and the radially distributed hydride or thickness of hydride rim is unscathed for the investigated time range. This implicates that ingress of hydrogen evolving due to dissolution of existing hydrides is negligible compared to ingress of fresh hydrogen in solid solution at this temperature. However, the morphological changes in hydride rim and its redistribution are observed depending on the temperature and annealing holding time above 600 °C. The complete dissolution of radial hydride rim takes 600 s at 600 °C, 60 s at 700 °C, and 0 s at 900 °C, beyond that concentration of hydrogen becomes uniform. The dissolution of hydride rim and subsequent redistribution and reorientation of hydrogen are explained by the phase transformation of Zircaloy from the $\alpha + \delta$ phase to the $\alpha + \beta$ or β phase which greatly enhances the terminal solid solubility and hydrogen ingress in the Zircaloy matrix. After performing micro-hardness test, it is found that radial hardness varies with redistribution of hydride, recrystallization of Zircaloy and its phase transformation [69]. Thermotransport of hydrogen or flux of hydrogen due to redistribution of hydrides in response to applied thermal gradients was investigated for Zircaloy-4. The determination of heat of transport, energy required per mole for the hydride dissolution, is another way of quantifying the process of hydriding and its subsequent reorientation. Hydrogen existed in two dissimilar regions: single-phase region and two-phase region during thermotransport, and its distribution in these two regions has a smooth curve at their interface in contrast to that of anticipated a sharp

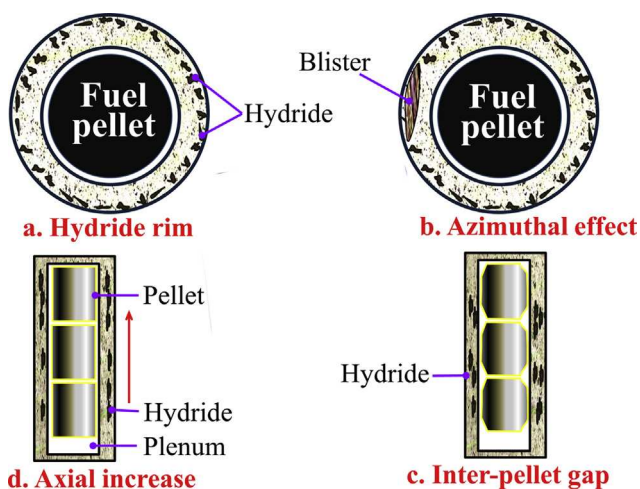


Fig. 9 – Hydride redistribution induced by temperature gradients.

discontinuity. The value of heat of thermotransport is reported to be approximately 30 kJ/mol [70].

A number of studies have been done to parameterize stress-induced reorientation of hydrides in Zircaloy. The reorientation of hydrides in radial direction under influence of circumferential loading is highly prominent during cooling of Zircaloy cladding from 573 K to 473 K. However, the reorientation of hydride is less frequent while cooling under circumferential loading either in lower temperature range (cooled from 473 K to 373 K) or in higher temperature range (cooled from 673 K to 573 K). This study testified that reorientation of hydrides, transformation of circumferential hydrides into radial hydrides after re-precipitation, is favoured by increase in loading time for a given temperature. A hydride concentration gradient in the direction of inner surface of cladding tube is observed [67]. The exploration of in situ tensile loading in hydrided Zircaloy-4 cladding tube revealed the presence of contrarily high strains in the hydride phase aligned with loading direction. The presence of such high strains in hydride phase failed to be deciphered on the basis of trivial elasticity theory and may be explained by a strain-induced ordering of hydrogen mechanism in the Zircaloy matrix. The strain-induced ordering that causes a transformation of δ -phase hydrides to γ -phase hydrides within the grains orientated in loading direction [71]. There is a threshold value of stress below which the hydrides are insensitive to external stress and hence exhibits no reorientation. The threshold stress for the hydride reorientation is a function of yield strength and temperature of the Zircaloy cladding sample. It increases with increase in yield strength and decreases with increase in temperature. The threshold stress for hydride reorientation is found to be 90 MPa at 508 K and 60 MPa at 673 K [72,73].

Zirconium hydride also reorients itself in the matrix in response to thermo-mechanical loading due to combined effect of stress and presence of hysteresis between heating and cooling curves. In contrast to isothermal condition, the effect of thermal cycling is more profound for the reorientation of hydride. The fraction of reoriented hydride and the hydride size increase hugely while cycling above the threshold stress value while a decrease in the measure of reoriented hydride is observed on increasing hydrogen content above 200 weight ppm. For the hydrogen content in the range of 200–300 ppm, above 90 per cent of hydrides get radially orientated after 12 thermal cycles; however at higher hydrogen content of 600 ppm, only 20 per cent of radial hydrides reorientation is observed. The precipitation temperature during the reorientation of hydrides is only slightly influenced by cycling effect and hydrides reoriented above threshold value of stress precipitate at a lower temperature compared to circumferential hydrides precipitated in a stress relieved sample. The state of hydride strain is different for redistributed hydrides and primary precipitated circumferential hydrides. The reoriented hydrides are observed to be reluctant to absorb thermal contraction of proximate zirconium grains in contrast to primary circumferential hydrides. Metallographic techniques have been used on samples of Zircaloy-4 before and after thermo-mechanical cycle for the determination of threshold stress for hydride reorientation. After the re-precipitation, the hydrides are seen to reorient in the perpendicular direction of

applied stress direction. The threshold stress value for the Zircaloy samples under investigation is reported to lie in range of 75–80 MPa. Hydrides preferentially precipitate in α -phase Zircaloy matrix with their c -axes inclined away from the hoop stress direction at an angle of 15–20°. However, under the influence of external stress, this preference is altered to precipitation in α -phase with c -axes stretched in the direction of external stress. The distances between interatomic planes of hydride are compressed and stretched, respectively, on the plane of the platelet and in perpendicular direction to this plane [67,74–77].

The extent of hydrogen degradation of Zircaloy is dependent upon not only on the fraction of hydride present but also strongly on the orientation of hydride with respect to applied stress. Circumferentially orientated hydrides may have strengthening effect marginally. Nonetheless, it causes a slight decrease in ductility of Zircaloy tubes. Isolated long circumferential hydrides are more detrimental to the ductility of Zircaloy clad tubes in contrast to strewn circumferential hydrides. Neither the activation volume nor deformation mechanism is significantly altered by the presence of circumferential hydrides. The dislocation intersection mechanism, according to which the accretions of foreign elements at the sites of dislocations disturb the activation length, forms the basis of understanding of the rate-controlling mechanism of deformation. The thermal cycles cause circumferential hydrides to reorient itself as radial hydrides. For the Zircaloy-4 cladding sample with 200–300 weight ppm of hydrogen, above 90 per cent of hydride reorient itself as radial hydrides after thermal cycles. After performing uniaxial tension test at ambient temperature on Zircaloy-4 cladding sample with 130–600 weight ppm of hydrogen, it is concluded that influence of radial hydrides on the axial ductility is inconsiderable. However, the increase in radial hydrides affected the overall mechanical properties. The critical level of radial hydrides for brittle fracture of Zircaloy-4 cladding tubes firstly increased with increase in hydrogen content (up to 300 ppm) and further increase in hydrogen concentration resulted in decrease of the critical level of radial hydrides required for brittle fracture. The threshold hoop stress required for the re-precipitation of circumferential hydrides into radial hydrides at 673 K in non-irradiated and high-burnup Zircaloy-4 fuel claddings samples are 80 ± 10 MPa and 75 ± 12 MPa, respectively. A small amount of radial hydrides can be extremely detrimental to the integrity of cladding materials of higher hydrogen concentration, although they are difficult to be formed [78–80].

Even though phenomenon of hydride blisters was first reported in 1977, a very few studies have been conducted on it. After a thorough characterization of hydride blisters developed on pre-hydrided Zircaloy-4 clad tubes by thermodiffusion method, it was revealed that blisters reach a thickness of 290 μm in a day. The existence of hydrogen gradient in the blisters is observed with δ -phase hydride being in nearby to the outer surface up to over 33 per cent of the blisters thickness. The core of the blister is subjected to compressive stresses while the bulk under it is subjected to the tensile stresses during its growth. The presence of this stress gradient causes further diffusion of hydrogen into it. However, the role of this stress gradient in the growth of blister is negligibly small compared to the thermal gradient. The existence of

diffusion equilibrium threshold is proposed as a limiting criterion for blister growth and it is suggested that hysteresis in the terminal solid solubility of hydrogen in the Zircaloy matrix must be incorporated in order to model thermo-diffusion of hydrogen in Zircaloy. In another study on blistering, two different types of blister morphology are identified. First type of blister is in isolation, round in shape and positioned at the cold spot region whereas the second type of blister is the amalgamation of numerous small blisters in a ring like structure in the vicinity of the cold spot. The blisters are found to have three different regions: only hydrides, sample matrix combined of radial and circumferential hydrides, and matrix only with circumferential hydrides. Amount of hydrogen and overall sample temperature strongly influenced the blisters growth. The shape of blisters is seen to be dependent upon the local temperature field; however, its other characteristics such as depth, volume are influenced by bulk conditions of sample. It is stimulating to see how hydrides present in the vicinity of blisters respond to its formation and what its impacts on the Zircaloy sample are. It is noticed that even in the absence of external stress; hydrides reorient themselves radially to the blisters. The pre-circumferential hydrides around the blisters constrain the length of the reoriented radial hydrides, however, they increase their reach. On the application of external stresses in circumferential direction; blisters act as a stress concentrator which give rise to a stress gradient in its neighbourhood and cause further hydrogen diffusion, forcing radial hydrides to grow laterally and transversally (both length and thickness) [81–83].

In spite of widely acknowledged phenomenon of redistribution and reorientation of hydrides, there is a deficit of investigation performed with irradiated Zircaloy tube. The relevant results reported are, by and large, scattered and there is no clear parametric demarcation either in terms of hydrogen content, sample bulk temperature, or stress threshold value for the redistribution or reorientation of hydride phases in Zircaloy clad tubes. There is also a lack of understanding of stress proliferation within the hydride phases and its influence on its own redistribution and reorientation. The phenomenon of blistering and its impacts on Zircaloy-4 cladding need further investigations in order to develop better understanding about the role of terminal solid solubility hysteresis in the formation of blisters, blister formation threshold, widely agreed morphology of blisters etc.

Impacts of hydride

Since radioactive fuel is encapsulated by Zircaloy claddings, its integrity is of utmost importance not only during normal and off-normal reactor operation but also during shut down or intermediate storage period. The mechanical properties and fracture toughness of Zircaloy clad tube degrade drastically with precipitation of brittle hydride phases in zirconium matrix. As it is evident from the previous discussions that the phenomenon of hydriding is multifaceted and dynamically evolving which in turn not only makes the assessment of degradation of Zircaloy clad tube integrity an intricate task but also exacerbates the susceptibility of its integrity during reactor service as well as storage. An extensive amount of

studies have been performed in order to understand the nuances of hydrides' impacts on Zircaloy tube integrity. In light of all these studies; the phenomena of degradation of clad integrity due to presence of hydride may be stratified into three intimately connected layers: Creep, Crack and Fracture. Ambient settings such as temperature and corrosive atmosphere govern crack growth. At a high temperature, in order of about half of melting point, metals show crack growth through creep i.e. slow growth of crack even at constant load. Circumambient conditions of high temperature and corrosive environment (pivotal for hydriding), similar to which fuel cladding is exposed, influence crack growth through creep which leads to fracture eventually; thereby making an intimate nexus of these three phenomena along the lines of creep effectuates crack growth leading to fracture [84]. The impacts of hydrides on creep, crack growth and its propagation, and fracture toughness are discussed below separately, with occasional overlap of territory.

Creep is the inelastic response of any materials operating at high temperatures. Creep in Zircaloy at high temperatures is due to enhanced diffusion of hydrogen atoms as well as increased mobility of dislocations and it is contingent on the microstructure, texture, hydrogen content etc. In order to apprehend the influence of hydrogen content in range of 0–185 weight ppm on creep characteristics of Zircaloy with grain size 20–50 μm , an indentation creep study of zirconium hydrogen solid solution was conducted. At temperature of 693 K and for stress range of 100–200 MPa; the exponent n of power-law creep (dislocation creep) is 3.26. This power-law creep exponent is independent of increasing hydrogen content and exhibits the dislocation climb creep behaviour. The diffused hydrogen escalates the creep rate by modifying the Young's modulus, and not by altering the creep mechanism. In another similar investigation, it is reported that creep rate is accelerated with increase in concentration of hydrogen in both transverse and longitudinal directions. At the temperature of 723 K for the hydrogen content of 160 weight ppm, the surge in creep rate is approximately 2–2.5 times in both the directions. After probing thermal creep phenomenon at 673 K in both cold-worked stress-relieved and recrystallized types of Zircaloy-4 tubes with corrosion-induced hydrogen content in the range of 16–756 weight ppm, it is stated that diffused hydrogen decreases the creep rate in cold-worked stress-relieved Zircaloy-4 but increases the creep rate in recrystallized Zircaloy-4. The presence of hydrides decreases the creep rates by about 33 per cent compared to virgin cladding tubes. The effect of hydrogen ingress on the creep rate before and after the terminal solid solubility is opposite in the recrystallized Zircaloy-4 tubes [85–87].

Crack growth depends on loading conditions and environmental conditions. It may be extremely fast, over 1000 m/s, and it may be extremely slow, less than 1 mm/year. Hydrided thin-wall Zircaloy sheet is examined for crack growth in the through-thickness direction for the temperature range of 298–648 K. At 298 K, growth of crack followed the radially orientated hydrides if these are present at the tip of the crack. If the tip of the crack came across in-plane hydrides, crack growth initiation occurs due to creation of primary voids at fractured hydride sites and it propagates by coalescence of the crack tip with hydride-induced void in the front of it. In higher

range of temperature i.e. at 573 K and 648 K, the extension of crack happens because of crack-tip blunting as the resistance to crack-growth initiation is high enough [88]. The cracking behaviour of Zircaloy-4 is strongly dependent upon the grain size; the cracks are small and independent for the grain size less than 30 μm whereas the cracks become larger and grow in radial direction in case of grain size greater than 500 μm . The precipitation of hydrides causes not only large cracks but also small bulges [89]. After the in situ observation of crack propagation in small specimens of hydrided Zircaloy-4 placed under the scanning electron microscope, it is noticed that cracks propagate by macroscopic stable crack growth mechanism and the resistance curves decreased with increase in hydrogen content. Orientation of the precipitated hydrides influences fracture toughness; and higher values of toughness due to plastic deformation are seen for the hydrides precipitated normal to the crack. The effect of orientation of hydrides and the presence of hydrogen concentration gradient at the tip of the crack are examined. The fracture behaviours are brittle fracture without any prior stable crack growth at the ambient temperature, brittle fracture with some previous stable crack growth at 323 K, and ductile at high temperatures for the anisotropic distribution of hydrides. However, the fracture mode is always ductile for homogeneous distribution of hydrogen. The transition of fracture behaviour from ductile to brittle takes place when hydrides are localized at the tip of the cracks and orientated parallel to crack plane at the low temperature [25,90].

The Zircaloy fuel claddings do not only act as a safety barrier to release of radioactive fuel to the coolant but also are interface for transferring of heat liberated by fuel undergoing fission to coolant. Clad tubes are manufactured as thin-walled tubes having thickness of about 0.4 mm in order to maximize the heat transfer. Because of such less wall thickness, it is impracticable to assess the fracture behaviour of Zircaloy fuel claddings as per the 'ASTM International' test techniques. Nevertheless, the data pertaining to valid fracture mechanics parameters are essential in order to analyze the structural integrity of claddings. Several studies have been undertaken for the assessment of these parameters by impoverishing the test technique for such thin claddings [91]. The measurements of fracture toughness for both stress-relieved and recrystallized Zircaloy-4 with hydrogen content of 300 weight ppm was conducted by making X-specimens. The recrystallized Zircaloy cladding sample demonstrated superior fracture toughness to stress-relieved sample at all temperatures. It may be due to the fact that after the recrystallization and anneal treatments, the larger grain size of α -phase would improve the ductility of Zircaloy-4 hence its fracture toughness. Precipitation of hydrides decreased fracture toughness in both types of Zircaloy-4 samples. However, impact of hydrides presence is more severe in case of stress-relieved specimens. For stress-relieved Zircaloy-4, the cleavage fracture and secondary cracks are seen to be a result of continuous circumferential hydride strings; while in case of recrystallized Zircaloy, the voids are induced by the discontinuous hydride strings. The effects of hydride are more prominent at low temperature as rise in temperature causes mitigation of hydrogen embrittlement. The fracture toughness of recrystallized Zircaloy-4 degrades with increase in hydrogen content at all range of

temperature investigated. In recrystallized Zircaloy-4 for higher hydrogen content of about 800 weight ppm, highly localized hydrides in the form of hydride rim or blisters are the preferable crack initiation sites [92,93]. The fracture toughness test on commercially available Zircaloy-4 was conducted to determine the influence of hydrogen content in the temperature range of 293–473 K. At the ambient temperature, the dominating failure mode is ductile with very few sample exhibiting brittle failure and that too at high hydrogen content. Hydrogen content intensely governs the micro-mechanisms of fracture in Zircaloy-4. Ductile fracture occurs due to creation and propagation of voids for low hydrogen content whereas brittle fracture is dominant for higher hydrogen content. The fractured surfaces were also examined to correlate the effect of precipitates density and the hydride phases, and following three different stages are observed – (i) For hydrogen content less than 25 ppm: few precipitates and no hydride, (ii) For hydrogen content up to 250–350 ppm: precipitates density increased rapidly implicating that these guide the fracture path, (iii) For higher hydrogen content: precipitates density diminished and hydride phase grew, suggesting that brittle phase determined the direction of crack growth propagation [94]. Similar observations are made in another study conducted to assess the influences of temperature and hydride on fracture behaviour of Zircaloy-4. At ambient temperature, the toughness value for cladding samples decreases with increase in concentration of hydrogen. However, the gap in fracture toughness values of virgin and hydrided Zircaloy samples is small at higher temperature about 573 K. During reactor operation, hydrides redistribute and reorient themselves as discussed in previous sections. The orientation of hydrides too plays a significant role in deciding the fracture toughness of Zircaloy. At room temperature and 300 weight ppm of hydrogen content, the fracture toughness of radial hydrides is less than circumferential hydrides. This is attributed to degrading properties of radial hydrides by facilitating crack propagation. At higher temperature about 573 K, in spite of having different surface morphologies, the toughness value for both radial hydrides and circumferential hydrides is comparable. Another extensive examination assessing the dependence of the fracture resistance on hydride reorientation revealed that fracture of reoriented hydrides with larger sizes ($>10 \mu\text{m}$) is more dominant than that of smaller sized reoriented hydrides. Reorientation of hydrides diminishes the fracture resistance by the mechanism of void nucleation, growth and propagation through coalescence phenomenon at the tip of the crack. Fracture of reoriented hydrides causes nucleation of voids which enlarge due to plastic blunting. High cooling rate across the solvus range of temperature is suggested for moderating embrittlement effect due to reoriented hydrides [95–97]. Hydride blisters, which are typically elliptical or lens shaped, are the result of massive localized hydriding in Zircaloy fuel cladding in zone of low temperature. They are comparatively thicker and penetrate almost half of the tube thickness. The hydride blisters are brittle for all the test temperatures in the range of 25–400 °C. A large number of cracks develops and propagates via blisters almost immediately after the yielding of plastic region under the blisters. For a certain blister depth, the material ductility severely gets reduced at ambient temperature

compared to that of at higher temperature. The propagation of crack nucleated within the blisters at room temperature may be anticipated using elastic–plastic fracture mechanics. Further in the absence of blisters or with blisters less than 50 μm , a prominent reduction in ductility is induced with increase in biaxiality level. The fracture strain decreases rapidly at room temperature and decreases steadily at higher temperature with the depth of blisters [98,99].

Zircaloy-4 fuel clad tubes are exposed to stress for a long period time of time at high temperatures; under such scenario creep is crucial phenomenon and their thorough understanding is of paramount importance. However, high cost and large amount of time involved in conducting creep tests make it difficult to experimentally assess the creep behaviour of Zircaloy. There is want of investigation on creep behaviour of Zircaloy-4. The nucleation or initiation of crack and their propagation are extremely difficult to predict during in situ environment of clad tube. There have been several attempts to understand the influence of hydrogen content upon these phenomena, still more investigations on Zircaloy-4 under identical conditions are needed to firmly establish widely accepted mechanism and correlations. Even though the fracture resistance and its dependence upon hydrogen infusion for Zircaloy are extensively explored, there is a scope of more precise assessments in irradiated condition at higher temperatures and hydrogen content range exclusively for Zircaloy-4; as the literature is scattered due to studies conducted on different Zircaloy compositions.

Delayed hydride cracking

Zircaloy fuel cladding encapsulates radioactive fuel and it is removed from the reactor once the fuel inside it is not fissile enough to produce heat up to a level required to generate electricity; however, this decayed fuel continues to produce a substantial amount of heat even after the removal of cladding from the core. These fuel clad tubes with decayed fuel inside need to be continually cooled for many years in order to avoid its rupture caused by overheating, which can lead leakage of radioactive fuel in to the environment. In such a long time frame combined with increased tensile hoop stress compared to in-reactor operation, as a result of pre-storage drying transfer and early stage storage, presence of hydrides in Zircaloy fuel claddings causes its cracking through a phenomenon called delayed hydride cracking (DHC). This time-dependent process of hydride cracking, termed as delayed hydride cracking, is a sub-critical crack growth phenomenon based on the mechanism of ingress of hydrogen to an elevated tensile stress zone followed by nucleation, growth, and fracture of the hydrided region as shown in Fig. 10. The precipitation of hydrides at the higher stress zone as group of platelets having their normal parallel to maximum tensile stress is typical feature of delayed hydride cracking. However, delayed hydride cracking may take place even in absence of bulk hydrides. Since it is a time dependent phenomenon, there must be some time interval between the impositions of stress and beginning of cracking and this interval is termed as the incubation time. Cracking

of hydride is quick once the critical crack length is achieved but it takes time for regaining the critical conditions, hence it is intermittent in nature. The cracking initiates only when a threshold value of stress intensity factor is exceeded but this intensity factor has almost no influence on its propagation or crack velocity as evident from Fig. 10. The crack velocity v_c is influenced by the temperature, though dependency is too complex, and has an apparent Arrhenius behaviour given by $v_c = v_0 e^{-Q/RT}$; where Q is activation energy for delayed hydride cracking, T is temperature, R is gas constant and v_0 is constant [100]. The delayed hydride cracking propagation or velocity is crucial in understanding this time dependent phenomenon. The crack velocity measured in unirradiated Zircaloy-4 calculated using pin-loading tension technique followed the temperature dependence in accordance to above mentioned Arrhenius-equation till 275 $^{\circ}\text{C}$ and fall-off in rate beyond that. Striations are absent implicating that these are not fundamental characteristics of delayed hydride cracking [101]. Zircaloy-2 cladding tubes having hydrogen content in the range of 90–130 ppm were put under scanning electron microscope for the direct observation of crack propagation and thereby measuring the delayed hydride cracking velocity in the radial direction in the temperature range of 225–300 $^{\circ}\text{C}$. The crack velocity adheres to Arrhenius relation up to the temperature of 270 $^{\circ}\text{C}$ with the activation energy of about 49 kJ/mol. Delayed hydride cracking is not observed beyond 280 $^{\circ}\text{C}$. The critical stress intensity factor for the initiation of the crack propagation is in the range of 4–6 $\text{MPa m}^{1/2}$. As anticipated, cracks propagated in intermittent manner and gradually steady state is approached with increase in crack depth [102]. Fracture of hydride at the crack-tip is a necessary requirement for the propagation of a crack by delayed hydride cracking. The detailed micro-mechanisms of such fracture are not yet well understood as well as there is a lack of fresh experimental investigation on delayed hydride cracking in Zircaloy-4 under conditions similar to that of reactor core.

Better understanding of delayed hydride cracking is also a prime concern for new generation of nuclear reactors in which claddings are subjected to with high-burnup. Tests were conducted on high-burnup and pre-hydrided (hydrogen content about 520–620 weight ppm) Zircaloy-4 under simulated drying-storage conditions. The ductile to brittle transition temperature is found to be less than 20 $^{\circ}\text{C}$ and approximately 55 $^{\circ}\text{C}$ for the hoop stress of 110 MPa and 140 MPa, respectively. This transition temperature is dependent on cladding material, stress corresponding to highest drying-storage temperature, hydrogen content, and radially distributed hydride prior to storage conditions exposure. It is also seen for the same cladding material that differences in irradiation environment contribute to difference in vulnerability of radial hydrides precipitation during cooling. In comparison to high-burnup Zircaloy-4, high-burnup ZIRLO™ is found to be considerably more susceptible to radial hydride and consequently delayed hydride cracking. It is crucial for the fact that new high-burnup reactors are in transition of using Zircaloys other than Zircaloy-4. They may outshine the Zircaloy-4 in reactor operation but can be inferior during storage conditions where too safety is of utmost important [103].

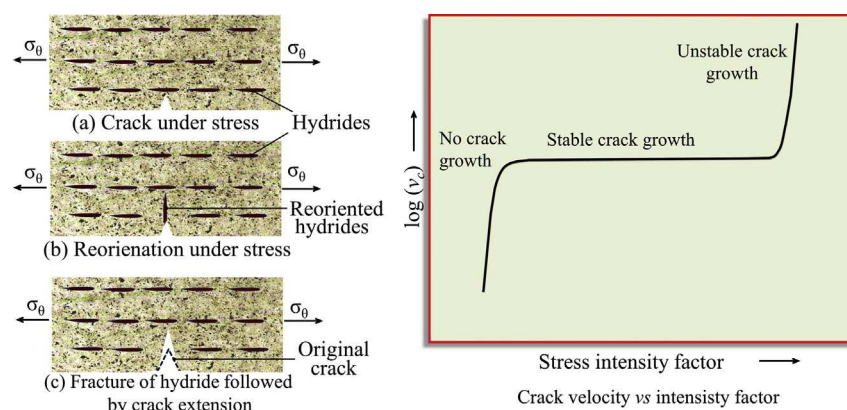


Fig. 10 – Stages in DHC and its propagation with stress intensity.

Models for phenomena associated with hydride embrittlement

Hydride embrittlement of a nuclear fuel clad is a very complex phenomenon because of various factors, namely internal factors like Zircaloy's microstructure, hydride redistribution and reorientation etc. and external factors like nuclear reactor core environment, influencing it heterogeneously. Given such complexity in situ experimental investigation is irrational and several attempts have been made to analytically and numerically investigate the various phenomena related to hydride embrittlement; few of them have been summarized in Table 5. Simulation based on these modelling produces results similar to that of experiments and is a sophisticated tool for analyzing the output on a desirable time and size scale. Modelling of these phenomena not only helps in better understanding of their mechanisms but also compresses the time frame and cut down the cost. However, experiments need to be performed in order to obtain the various reference parameters and behaviours as these parameters and/or behaviours are essential for modelling as well as its validation.

The ductility of Zircaloy is more often determined by the highest hydrogen zone, and thus for its evaluation, a precise temperature distribution along with a consistent model for hydrogen migration and precipitation is required. On the basis of diffusion and precipitation laws, one such model is developed in order to simulate the behaviour of hydrogen in Zircaloy-4 clad tube. It is found that hydrogen is accumulated on the colder region of clad due to Soret effect. Homogeneous solid solution of hydrogen is precipitated to form hydrides during the shutdown of reactors. Thickness of hydride rim depends upon the amount of hydrides per unit volume. A 60 μm thick rim is predicted for 1000–2000 weight ppm of hydrogen content. One of the limitations for this model is that it did not consider the oxide layer presence which is very crucial for the calculation of the temperature, especially at the oxide formation site like cladding/coolant interface [68]. A thermodynamic model for Zr–H is developed to find the terminal solid solubility, temperature, and partial pressure concentrations required for the precipitation of hydrides. Further predictions of this thermodynamics model are used as boundary conditions in a kinetic model based on finite element method to understand the redistribution of hydride

in a Zircaloy-2 sample. This model testifies the existences of hydrogen diffusion coefficient. Another thermodynamic model developed to study the reorientation behaviour of hydrides under stress gradient in Zircaloy-4 interprets that the critical stress for hydride reorientation is dependent upon solution temperature and specimen hydrogen concentration [74,104]. Based on the finite element method, a meso-scale model of the hydrogenated Zircaloy-4 is proposed to understand the effect of hydrogen content on its creep behaviour. This model shows considerable effects of hydride distribution and orientation on the creep behaviour which agrees well with the reported experimental results. This model also predicts that creep strain will be higher for large variation or higher randomness in spatial distribution of hydrides [105]. To understand the effect of hydrides precipitation on the outside-in-crack movement or instability, a finite element based method is proposed. This model claims that the size of hydrides would affect the crack stability; longer hydride platelet or long split in radial hydride accelerates the crack propagation [106]. Propagation of a crack is simulated using quasi-static method and embedded-atom type potential is elucidated in order to understand the effect of hydrogen atom on the deformation mechanisms and phase transformations occurring in the vicinity of tip of the crack. Simulations at atomic level revealed that twinning, dislocation emission and phase transformation in the neighbourhood of the crack tip take place during fracture of hexagonal close-packed zirconium at low temperature irrespective of the presence of impurities. Diluted interstitial due to hydrogen ingress near to tip of crack alters the size of the regions of phase transformations [107]. Fracture mechanics parameters such as plastic yield load, stress intensity factor etc., of hydrided Zircaloy-4 at an elevated temperature is probed using finite element method. These values are utilized for the estimation of failure stress of the Zircaloy cladding tube using failure assessment diagram. This failure assessment diagram predicted that failure load for cladding is approximately same for both hydrides, either localized under the surface or uniformly distributed circumferentially [108]. During finite element simulation of fracture of hydride modelled on the basis of de-cohesion crack growth mechanism, it is observed that fracture toughness decreases with increase in stress parallel to crack faces [109]. Strain fields in zirconium hydrides are the key in propagation of delayed hydride cracking. A finite element based model is

Table 5 – Models for phenomena associated with Zr–H system.

| Zirconium alloy | Range of parameters | | | Phenomenon of Zr–H system modelled | Technique/s employed | Outcome(s) | Ref. |
|------------------------|-----------------------------|---------------------|--|---|--|--|-------|
| | Temperature | H content | Others | | | | |
| Zircaloy-4 clad tube | | 1000–2000 (wt. ppm) | | Behaviour of H | Analytical method & BISON | <ul style="list-style-type: none"> ❖ Hydrogen accumulates on the colder spots of the cladding ❖ Shutdown has a limited effect on the hydride distribution | [68] |
| Zircaloy-2 | 138.8 (K cm ⁻¹) | 130 (wt. ppm) | | Hydrogen redistribution | Finite element method & Thermodynamics model | <ul style="list-style-type: none"> ❖ Confirms the presence of hydrogen diffusion coefficient ❖ Indicates virtually pure H₂ is needed to produce hydride | [104] |
| Zircaloy-4 clad tube | 473–573 (K) | 100–600 (wt. ppm) | Thermal cycles: 0–12 | Hydride reorientation | Thermodynamics model | <ul style="list-style-type: none"> ❖ Threshold stress for hydride reorientation is function of solution temperature and hydrogen concentration | [74] |
| Zircaloy-4 sheet | 623–693 (K) | 250–500 (wt. ppm) | σ : 80–130 (MPa) | Creep behaviour | Finite element method | <ul style="list-style-type: none"> ❖ Distance between hydrides has crucial role in fracture ❖ Kinked cracks are detrimental in non-radial cracks | [105] |
| Zircaloy cladding | | | Hydride length: 0.1–0.3 mm | Crack instability | Finite element method | <ul style="list-style-type: none"> ❖ Radial-hoop-radial cracking path would be a good approach to account for the DHC degradation behaviour. | [106] |
| Zr-HCP unit cell | | 0.27 (wt. ppm) | Direction $\begin{Bmatrix} 1\bar{1}00 \\ 0001 \\ 1\bar{2}00 \end{Bmatrix}$ | Crack propagation & atomic interactions | Quasi-static method & embedded atom type | <ul style="list-style-type: none"> ❖ Twinning, dislocation emission and phase transformations transpire near the crack tip zone during low temperature fracture ❖ Interstitial H near crack tip modifies phase transformation size | [107] |
| Zircaloy-4 clad tube | 620 (K) | 10–387 (wt. ppm) | | Fracture behaviour | Finite element method | <ul style="list-style-type: none"> ❖ Failure load is equal for hydride accumulated locally under the outer surface and uniform distribution circumferentially | [108] |
| Zr–2.5Nb | 350–585 (K) | | | Hydride fracture | Finite element method & Analytical method | <ul style="list-style-type: none"> ❖ Fracture toughness decline with stress parallel to crack faces ❖ Reduction is more prominent at elevated temperatures | [109] |
| Zr–2.5Nb pressure tube | | 60 (wt. ppm) | σ : 650–949.5 (MPa) | Strain fields of hydrides | Finite element method | <ul style="list-style-type: none"> ❖ Hydride precipitation and parametrization of crack tip hydride microstructures should be incorporated in model | [110] |
| Zr–2.5Nb pressure tube | 420–600 (K) | 0.9 (at. %) | | Delayed hydride cracking | Analytical method | <ul style="list-style-type: none"> ❖ A positive temperature gradient accelerates DHC, enhances critical temperature at which crack stops while heating | [111] |
| Zircaloy-2 | 523 (K) | 0–200 (wt. ppm) | Hydride length: 0–10 μ m | Delayed hydride crack velocity | Finite element method | <ul style="list-style-type: none"> ❖ Stress distribution in vicinity of crack tip is significantly altered by precipitation of hydride | [112] |

used to characterize the precipitation of hydride at such stress locations. The result of model is compared with the X-ray strain mapping outcomes. It provides better understanding of intricate details that could have not been observed experimentally. Another mathematical model incorporated the temperature gradient effects on delayed hydride cracking in clad tube and concluded that positive temperature gradient accelerates the delayed hydride cracking. A finite element model studying the effect of δ -phase hydride precipitation on the velocity delayed hydride cracking predicted that it alters the stress distribution near the tip of the crack considerably and the crack velocity is the function of stress intensity factor, temperature, material strength etc. [110–112].

Conclusions

Hydrogen is the smallest possible atom and its ingress in Zircaloy fuel cladding beyond terminal solid solubility makes cladding vulnerable to failure by phenomenon called hydrogen embrittlement. Hydrogen or hydride-induced embrittlement is a multifaceted phenomenon and occurs via a number of phenomena occurring either simultaneously or in isolation. The researches pertaining to hydrogen embrittlement are highly scattered as well as with contradictory outcomes. The present article attempts to succinctly summarize relevant but scattered researches in order to develop simplistic and coherent understanding of this complex phenomenon. However, given the complexity of phenomenon as well as the presence of vast literature, it may not include every single findings but emphasis is on recent outcomes along with coherency. Following conclusions may be drawn:

- ❖ Hydrogen uptake by Zircaloy fuel cladding is influenced by various factors. In spite of large number of investigations in the past to establish a universally accepted mechanism for corrosion followed by hydriding of Zircaloy, there exists ambiguity. This may be attributed to varying conditions under which works have been undertaken by different researchers. There is a need for further exploration of this phenomenon under identical conditions for the better understanding in order to propose a universally accepted mechanism.
- ❖ There is no conclusive understanding of hydride precipitation and its actual phase identification and quantification. A number of habit planes, along which precipitation are preferred, are reported and there is a lack of agreement among these findings, which in turn makes very difficult to establish any fundamental mechanism for the crystallographic correlation between the Zircaloy matrix and hydride phases.
- ❖ There are ambiguities related to conditions at which the precipitation of γ -phase hydride occurs and also lack a clear demarcation for its detection.
- ❖ There are major challenges in order to precisely assess the stress evolution in Zircaloy cladding as well as in the hydride phases during in-reactor conditions. There is dearth of investigation on the microstructural development induced by irradiation as well as the mechanism of deformation under irradiation of Zircaloy-4.

- ❖ The phenomena of redistribution and reorientation of hydrides in irradiated Zircaloy tube need to be investigated more in order to develop understanding of in-reactor conditions.
- ❖ There is no clear parametric demarcation either in terms of hydrogen content, sample bulk temperature, or stress threshold value for the redistribution or reorientation of hydride phases in Zircaloy clad tubes. There is also a lack of understanding of stress proliferation within the hydride phase and its influence on its own redistribution and reorientation.
- ❖ The phenomenon of blistering and its impacts on Zircaloy-4 cladding need further investigations in order to develop a better understanding of the role of terminal solid solubility hysteresis in the formation of blisters, blister formation threshold, widely agreed morphology of blisters etc.
- ❖ There is need of more precise assessments of creep and fracture behaviour exclusively of Zircaloy-4 in irradiated, and higher temperatures and/or hydrogen content zones; as the literature is scattered due to studies conducted on different Zircaloy compositions.
- ❖ Fracture of the hydride in the vicinity of the crack-tip is a necessary requirement for the propagation of a crack by delayed hydride cracking. The detailed micro-mechanisms of such fracture are not yet well understood as well as there is a lack of fresh experimental investigation on delayed hydride cracking in Zircaloy-4 under simulated conditions similar to that of dry/wet storage.
- ❖ Modelling of phenomena related to hydrogen embrittlement is not only crucial in better understanding of their mechanisms but also compresses the time frame and cut down the cost. However, experiments need to be performed in order to obtain the various reference parameters and behaviours as these parameters and/or behaviours are essential for modelling as well as its validation, for example there is not well agreed value of hydrogen diffusion coefficient through oxide layer.
- ❖ No model has yet been developed that explain delayed hydride cracking initiation and propagation together. Even though few models describe the various essential features of delayed hydride cracking, all of them are highly idealized and in need of further refinement.

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