Hydride blisters formation, characterization and effect on the fracture of Zircaloy-4 cladding tubes under reactivity initiated accident conditions

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ABSTRACT

This work is part of the global research effort carried out at the CEA to improve the understanding of cladding failure under reactivity initiated accident (RIA) conditions, based on analytical mechanical testing techniques. The detrimental effect of hydride blisters, localized high hydrogen concentration zones, on the cladding resistance was observed in integral tests in dedicated research reactors. In order to better quantify this effect, a cold spot technique was developed to obtain hydride blisters in laboratory, and samples with blisters were tested at 25°C, 350°C and 480°C with a new mechanical test representative of RIA loading conditions named HB-EDC.

1 INTRODUCTION

During service exposure, Zircaloy-4 alloys used as PWR fuel claddings are oxidized by the water coolant. It results in the growth of an oxide layer (zirconia), and a fraction of the released hydrogen is absorbed and diffuses into the cladding. The zirconia is submitted to compression stresses due to oxide lower density than zirconium. It results in the development of cracks in the oxide due to micro-buckling. When the zirconia thickness reaches more than 100µm, these cracks may interconnect causing oxide spallation on a localized area (typically 1-5mm on the cladding outer diameter). Because hydrogen diffuses in thermal gradient, it could results in the development of localized high hydrogen concentration areas, named hydride blisters, on the outer diameter of highly irradiated Zircaloy-4 cladding. These zones are brittle. Blistering phenomenon was first observed in 1977[1] and blister induced failure in 1983[2], when an axial crack developed in a CANDU pressure tube following an array of hydride blisters on the external surface due to contact with the cold calendria tube. It was later shown in dedicated experiments in research reactors that blisters reduce the cladding ductility when submitted to a Reactivity Initiated Accident (RIA). One of the most critical hypothetical RIA scenarios is the Rod Ejection Accident. It corresponds to the unwanted remove a control rod from the PWR (Pressurized Water Reactor) core. It results in a fast power pulse transient that is intrinsically limited in time due to the Doppler effect of the uranium from the fuel pellets and the reduction of the moderator effect of the coolant water when the temperature increases.

The CEA Saclay has been performing studies to assess the cladding mechanical behavior for years. A specific program named PROMETRA[3] is devoted to characterize the cladding under RIA conditions, by uncoupling or partially uncoupling the different parameters that may affect the cladding mechanical resistance. This study is part of this program. This paper described a thermo-diffusion setup that was designed to generate hydride blisters on PWR Zircaloy-4 cladding in thermal conditions that optimized the blister growth rate. Then, it provides extensive experimental characterization of hydride blisters, such as their morphology, the hydrides crystallographic phases, or the hydrogen concentration inside and outside the blister. A newly developed mechanical test is presented. It allows improving the representativity of standard mechanical tests to RIA conditions. Eventually, the results of these mechanical tests performed at 25°C, 350°C and 480°C are presented and compared with previous study.

2 FORMATION OF HYDRIDE BLISTERS

Hydride blisters were artificially obtained in laboratory by reproducing the blistering scenario that may occurs in reactor [4]. First, cold-worked stress-relieved and unirradiated Zircaloy-4 claddings were hydrogen pre-charged at 300wppm by a gaseous charging technique. The initial hydrogen content was homogeneous on the cladding section. The cladding was then partitioned in 15, 20 or 30mm axial tubes. The samples were heated to dissolve a fraction of the precipitated hydrides, and a 1mm in diameter copper rod was simultaneously put in contact with the sample to generate a cold spot. This creates the thermal gradient necessary to trigger hydrogen thermal diffusion and to generate a blister.

Because many samples were required for subsequent mechanical tests, hydrogen thermodiffusion calculations were performed to define the best thermal gradient to apply to optimize the blister growth rate. The hydrogen diffusion in thermal and concentration gradient can be modeled by the equation 1 [5]:

$$J = -D\frac{dC}{dr} - \frac{DCQ^*}{RT^2}\frac{dT}{dr} \qquad (1)$$

where J is the hydrogen flux, D the diffusion coefficient of hydrogen in zirconium, C the hydrogen in solid solution concentration, Q* the heat of transport of hydrogen in zirconium, R the perfect gas constant equal to 8,314J/mol/K and T the temperature. The equation 1 was solved in 1D with a finite difference scheme implemented in Matlab. The procedure requires taking into account the solubility limit of hydrogen in zirconium because the term C is only the hydrogen in solid solution, not the total hydrogen concentration. Moreover, the solubility limit hysteresis was also taken into account. This means the solubility limit is not unique; it is lower in dissolution (TSSD – Terminal Solid Solubility in Dissolution) than in precipitation (TSSP – Terminal Solid Solubility in Precipitation) for a given temperature. Eventually, it was supposed hydrogen does not diffuse in hydrides. The implementation validity was checked by simulating the hydrogen profile obtained by Kammenzind [6] in a thermodiffusion experiment. It was chosen to do not overpass 380°C for the several hours thermal treatment to obtain hydride blister to do not restaurate or recrystallized the cold worked specimens. Then, a thermodiffusion calculation was performed to identify cold spot temperature that optimizes the blister growth rate. It was taken into account the diffusion situation was reach by cooling down the specimen from a higher temperature (385°C). The D, TSSD and TSSP parameter values identified by [6] were used, Q* = 25kJ/mol was fixed as an average of several authors reported values ([6-13]). The calculation was performed assuming spherical symmetry and logarithmic temperature variation (in lines with experimental observations). It was found cold spot temperature ranging from 200°C to 330°C allowed high blister growth rate.

The blister morphology obtained consists in a protrusion on the external diameter and a growth of a lenticular shape in the cladding thickness (figure 1). The blister depth reaches 217µm after 12h and 296µm after 24h. The square root fit of the blister depth in function of the thermodiffusion time gave depth = $6.4858\ t^{0.3335}$ with t in seconds. The reason of the protrusion is the hydrides lower density than the zirconium [14]. The ratio protrusion height to blister depth ratio was measured to be equal to 22.2% by metallography analysis on 4 samples. Post mortem analysis on 19 failed samples containing blisters showed the ratio is 21.5±1.2%, therefore confirming the ratio is about 22%. This ratio was used to check that the grown blisters correspond to the expected depth prior to mechanical testing by non-destructive measurement of the protrusion height. This also confirmed the good reproductibility of the developed setup in generating blisters. The figure 1 shows many hydrides are present under the blister. The hydrogen concentration is about 450wppm on the inner side to 1000wppm at the blister frontier based on measurement with the image analysis software HYDURO developed at the CEA. While Zircaloy-4 exhibit mainly circumferential hydrides (hydrides aligned with the tube circumferential direction) under standard reactor conditions, the figure 1 show a “sunburst” of radial hydrides around the blister. These radial hydrides are a clear mark of the stress field induced by the blister growth. The blister obtained microstructure is representative of some blisters observed in irradiated Zircaloy-4 claddings (figure 2).

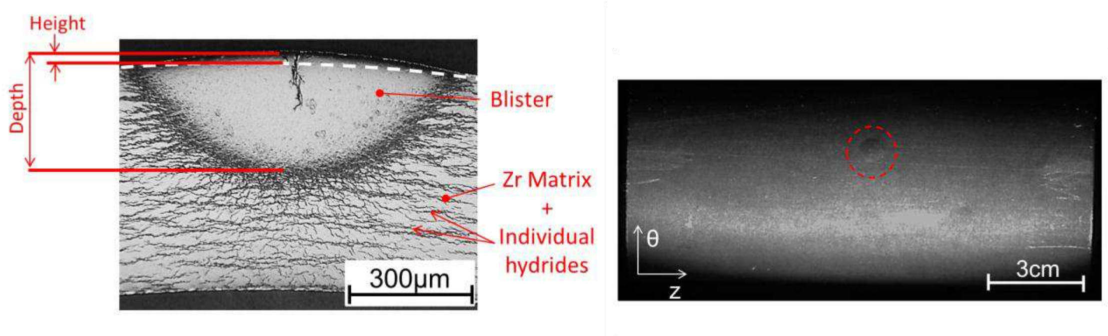

figure 1: Blister morphology in the radial circumferential plane and induced protrusion on the external surface (optical microscopy).

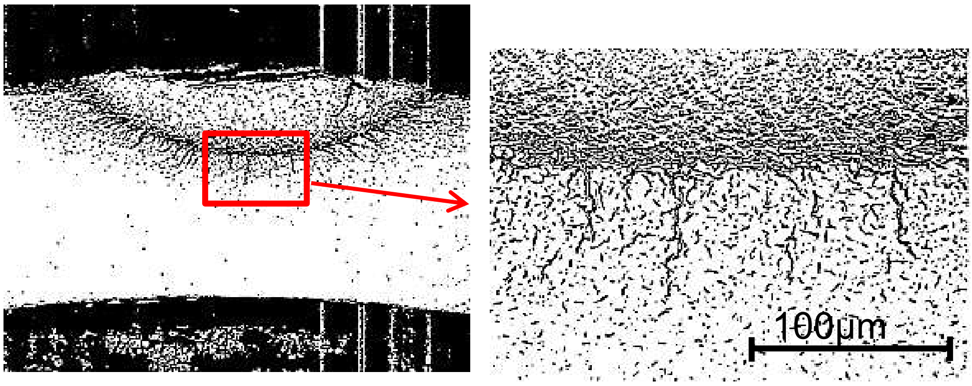

figure 2: Hydride blister in an irradiated Zircaloy-4 cladding [15].

Several characterizations such as X-Ray diffraction and micro X-ray diffraction in synchrotron, nano-hardness or micro-Elastic Recoil Detection Analysis (ERDA) were performed to measure the hydrogen content inside and outside the blister and the crystallographic phase of the hydrides in the blister. Only the ERDA measurements are detailed here for sake of brevity. ERDA is a nuclear technique well adapted for quantitative absolute measurement of hydrogen concentration [16]. Preliminary tests showed the accuracy at high content is about 2,5% on the hydride stoichiometry ZrHx. ERDA measurements showed the blister is a hydrogen concentration gradient mainly constituted of hydrides (more than 85% in volume fraction – figure 3). The concentration at the top of the blister is high enough for the transformation from zirconium to hydride to be complete. This result has been confirmed by XRD measurement in synchrotron, where peaks associated with zirconium completely disappeared in the upper area of the blister, and by nano-hardness measurements. All the hydrides were found to be "δ-hydrides".

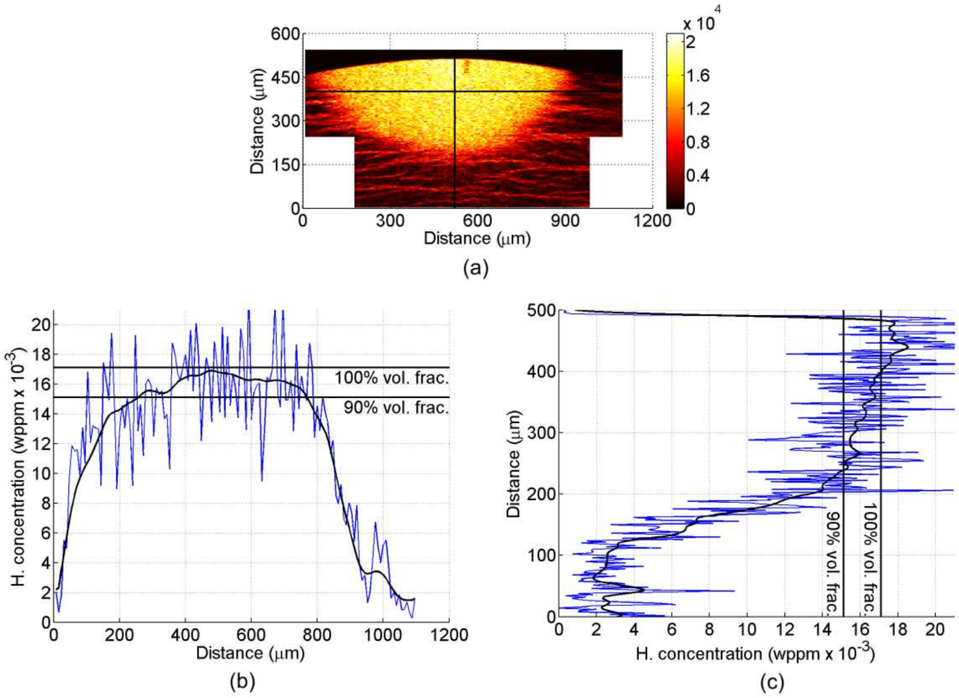

figure 3: Hydrogen concentration determined by ERDA (a) global cartography in wppm, (b) scan along the horizontal black line and (c) scan along the vertical black line.

3 DEVELOPPEMENT OF A NEW MECHANICAL TEST : HB-EDC

A newly developed test named High Biaxiality Expansion Due to Compression (HB-EDC) was developed to reach stress biaxiality ratio (axial to circumferential) of 0.5 while the standard EDC test biaxiality is limited to 0. The EDC test consists in compressing a soft pellet inside a tubular sample, to simulate the fuel pellet expansion (figure 4). The end of the sample are free to move axially, therefore no or very limited axial stresses are generated in the cladding. The basic idea of the HB-EDC is to block the axial displacement at the end of the sample (figure 4). Finite element computations showed this allows reaching a 0.5 biaxiality ratio that is more representative of RIA conditions where the biaxiality ratio is included between 0.5 and 1.

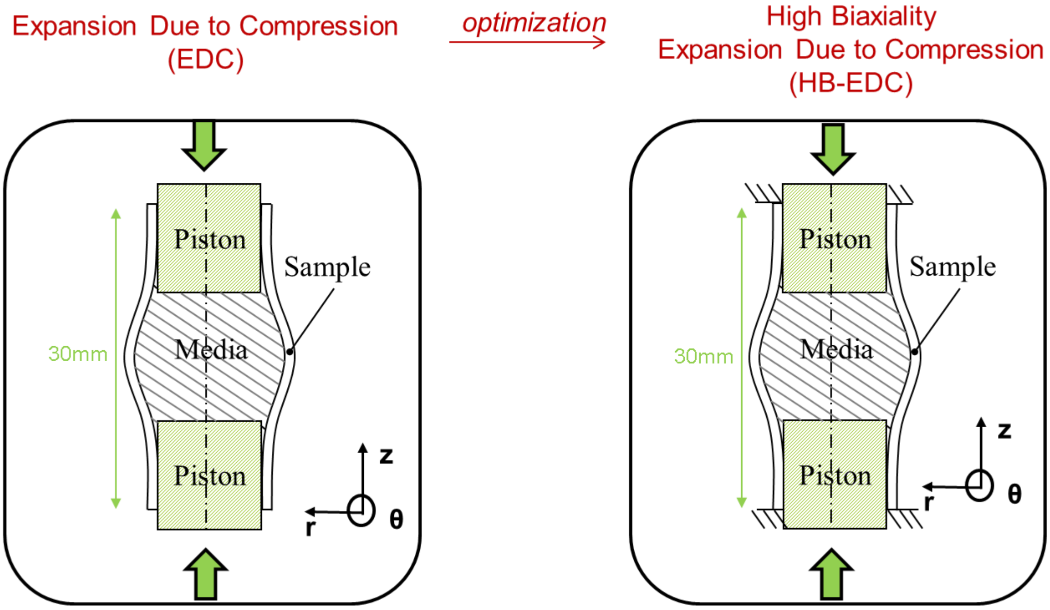

figure 4: Schematic view of EDC versus HBEDC tests.

The HB-EDC setup is easy to use, is reusable (more than 40 tests in the present study), requires only small samples (30mm long), allows to test samples with displacement controlled loading up to high strain rate, at high temperatures (up to 480°C in the present study but no part of the device limit higher temperatures), and is adaptable to standard tensile machine. The HB-EDC test has therefore all the characteristics needed to characterise the fracture of irradiated materials in shielded cells. It implementation in CEA shielded cells is planned in the near future.

4 APPLICATION OF EDC AND HB-EDC TEST TO STUDY THE LOADING BIAXIALITY INFLUENCE ON THE CLADDING FRACTURE WITH HYDRIDE BLISTERS

Several EDC and HB-EDC mechanical tests were performed at 0,1/s strain rate and 25, 350 and 480°C, monitored with an high speed optical camera (1000hz) to detect accurately the fracture of the cladding. The circumferential strain was measured as being the sample diameter on the last picture before cladding failure (figure 5). Zircaloy-4 cladding showed a marked influence of the loading biaxiality without hydride blisters. At 25°C, the fracture strain is divided by 2 to 3 between the EDC and HB-EDC. EDC tests at 350°C and 480°C without blisters did not allowed to produce samples failure while they failed at fracture strain from 20% to 30% with HB-EDC. This is illustrated by the figure 6(a) were the final aspect of EDC and HB-EDC after a 350°C test without blister can be observed. The presence of blisters clearly embrittle the cladding, as one could see on the sample post mortem aspect on the figure 6(b). Nevertheless, the loading biaxiality seems to have a limited or no effect on the fracture strain in presence of blisters (figure 5). This result is in lines with the previous observations of Glendening [17] who have reported no effect of biaxiality between biaxiality ratios of 0.5 and 1 in the fracture strains of Zircaloy-4 sheets.

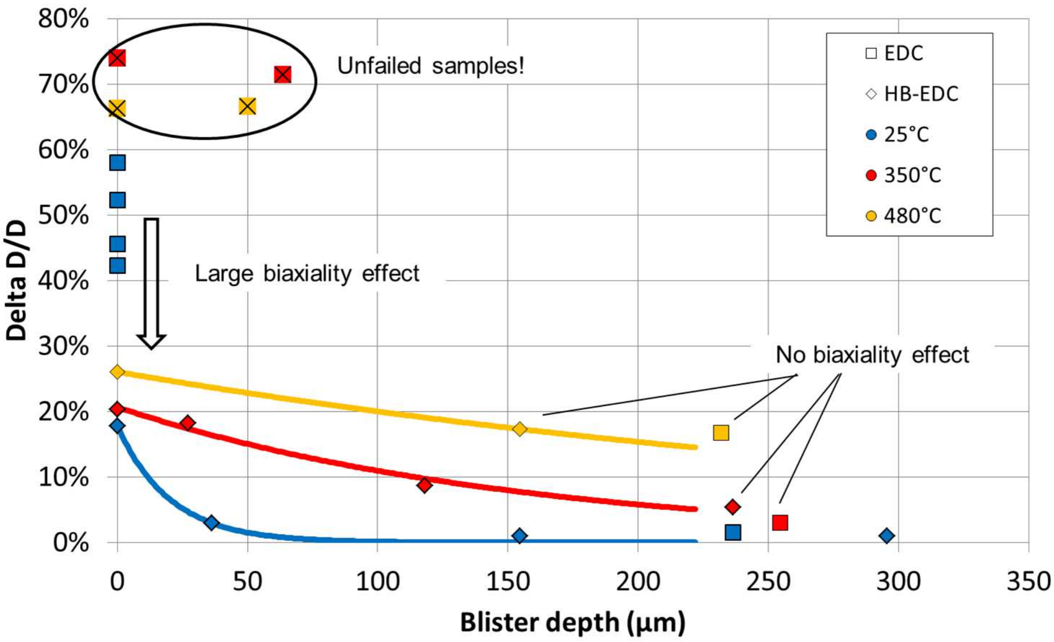

figure 5: Circumferential deformation measured with the last picture before fracture of EDC and HB-EDC tests at 25, 350 and 480°C, without blister or for different blister depths.

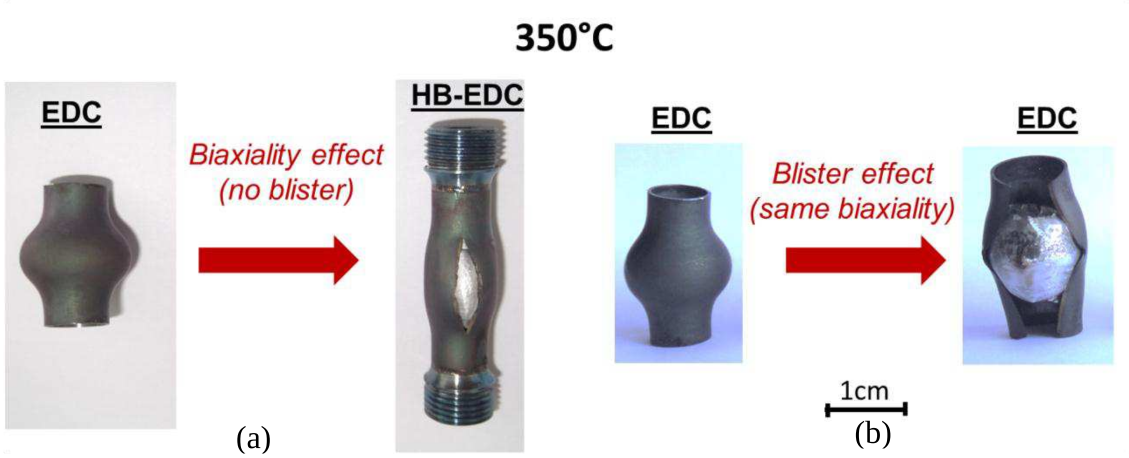

figure 6: Post-mortem aspect of (a) EDC and HB EDC sample without blister tested at 350°C and (b) aspect of EDC test without or with a 250µm deep blister at 350°C.

5 CONCLUSION AND PERSPECTIVES

A setup was developed to generate hydride blisters on Zircaloy-4 claddings. Preliminary thermodiffusion calculations were performed to determine the best thermal conditions to optimize the blister growth rate. Hydride blister cladding half-thickness deep were obtained in 24h. Extensive characterization of hydride blister has shown blisters are representative of some blisters observed in irradiated Zircaloy-4 claddings. A blister is a hydrogen gradient, where the complete transformation of zirconium to hydride can be achieved. A new mechanical named HB-EDC was developed. It allows performing tests on tubular samples and has all the characteristics needed for use on irradiated materials in shielded cells in the near future. The results obtained comparing EDC and HB-EDC tests showed a mark effect of the loading biaxiality without blister, but a negligible effect in presence of blister. Even in presence of deep blister (>200µm), the unirradiated material can maintain a certain ductility (≈4 to 5%) at 350°C.

This work has several perspectives. The very first step is to perform numerical computations to simulate the blister induced embrittlement.

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