EFFECTS OF THE HYDRIDE CONCENTRATION AND THE NEAR CRACK TIP GRADIENT ON THE FRACTURE TOUGHNESS OF ZIRCALOY-4

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ABSTRACT

The influence of concentration and distribution of hydrides as well as temperature on the fracture toughness of a Zircaloy-4 commercial alloy was studied in this work. Toughness was measured on CT specimens and the analysis was performed in terms of the J-integral resistance curves. The specimens were fatigue pre-cracked and hydrogen charged before testing them at different temperatures in the range of 293 to 473 K. The influence of a homogeneous hydrogen distribution was compared to a hydride concentration at the crack tip due to the presence of a mode I stress state during the H charge. The influence of the H content reducing the material toughness was important even at very low concentrations, being partially restored when the test temperature increased. The specimens charged under Mode I load presented reduced toughness values, and also fractured in brittle mode. The existence of a ductile-to-brittle transition is discussed.

1 INTRODUCTION

Zirconium (Zr) alloys are the major structural materials within the fuel region of a nuclear reactor. They are mainly used in the fuel cladding and fuel channel. The working environment of these components during operation is a combination of temperature and reactive conditions such as irradiation, oxidation and hydrogen (H) incorporation. At the operation temperature of a reactor, the terminal solid solubility of hydrogen in Zr alloys is low (about 130 ppm-H wt. at 623 K, Vizcaíno [1]) and further H absorption leads to the formation of zirconium hydrides. These hydrides are brittle and degrade the mechanical properties of the material. The extent of hydride embrittlement depends not only on the quantity of the hydride phase, but also on the hydrides morphology and their orientation in relation with the applied stress. Zirconium hydrides (ZrH) have received much attention as a fracture initiator because of their brittle behaviour and the thin platelet morphology of the δ phase (Ells [2]), phase which is found in most fractured components. The precipitate orientation is close related to both the material texture and the stress state at the precipitation zone.

The commonest way to study the effect of H on the mechanical properties of Zr alloys is by charging the material aiming at a homogeneous distribution of hydride concentration, and then testing it. The hydride distribution in cracked in-service components, instead, can be far from homogeneous because the stress gradient around the crack tip affects the precipitation process.

A study of the effects of H on the elastic-plastic fracture toughness of a unirradiated Zircaloy-4 commercial alloy at different temperatures is presented in this work. The influence of the distribution of hydride precipitates produced by H charging the

precracked specimens under Mode I loading was also examined and compared to the behaviour obtained at similar hydrogen homogeneous content. The existence of a ductile-to-brittle transition is discussed.

2 MATERIAL AND METHOD

Specimens were obtained from a Zry-4 rolled commercial plate 6mm thick. The plate fabrication process included hot-rolling, cold-rolling, annealing and conditioning. The main alloying elements and impurities obtained by chemical analysis are shown in Table I. The final material microstructure was α−Zry-4 fine equiaxed grains with a mean diameter of approximately 8μm. Laminated Zry shows an anisotropic mechanical behaviour caused by its characteristic texture (Tenckhoff [3]). Measurement of material texture showed that the c-axis was concentrated in the normal-transverse plane with maximums at 0º and 36º from the normal. The main mechanical properties were ultimate tensile stress (σ_{UTS}) 522 MPa and 510 MPa, yield stress (σ_{ys}) 365 MPa and 460 MPa, and elongation (ε%) 27.8 and 26.6, measured at room temperature in the rolling and transverse directions respectively.

Table I: Chemical composition of used material

Alloying elements (Wt%)					Main Impurities (ppm)			
Fe	Cr	FeCr	S	O	Al	C	Hf	Si
0.21	0.1	0.31	1.42	0.125	25	110	52	39

Compact tension (CT) specimens were machined to final nominal dimensions: W of 25.4 mm and B of 6 mm with notches oriented transversely to the rolling direction. All specimens were fatigue pre-cracked to a/W ratios between 0.45 and 0.55. Specimen dimensions followed ASTM E 1820-99 [4], with W/B of 4.23 (higher than the W/B=2 preferred ratio).

The specimens were hydrogen charged with the objective of obtaining two different types of final hydrogen distribution, a homogeneous distribution in the volume and a distribution with a high concentration at the crack tip. In order to do so, two consecutive methodologies were applied in both situations; first, an electrochemical technique, and second, an annealing treatment inside a hydrogen or argon rich atmosphere. Electrochemical charge was typically carried out at room temperature in a solution of 0.1M KOH with a current density of 10 mA/cm^2 during a period of time determined by the final concentration desired. The annealing process was performed at 720 K at hydrogen (argon) pressure ranging from 1.5 to 3 bar. Then, the specimens were slowly cooled in the furnace. Time and current density in the first technique, and time, temperature and H(Ar) pressure in the second, were the experimental parameters that allowed to obtain a wide range of final H contents. A LECO™ hydrogen analyser was used to measure this value. In order to have a heterogeneous hydrogen distribution, the hydriding process was performed on specimens (pre) mechanically loaded. This process consisted in loading the specimen on a test machine until a desired stress intensity factor value (K_I) is reached, then, by using a simple wedge, the imposed displacement was maintained

after removing the load. Some load relaxation was observed at this point, so the effective K_I was slightly lower than the imposed.

For tests performed at high temperature, specimens were heated by using two strip heaters. Temperature measurement and control were performed by means of a thermocouple with each wire welded to each specimen side, close to the crack tip. Therefore, only the zone close to the crack tip was heated. This methodology, introduced by McCabe and Landes [5], avoids heating the entire specimen plus the grip assembly, simplifying the experimental procedure.

All specimens were tested following ASTM E 1820-99 standard, the J-R curves being evaluated by means of the single-specimen unloading compliance technique. After the test, the specimens were fatigue post-cracked to delineate the stable crack growth. The tests were performed at 293, 343, 393 and 473K. Since the compliances were not measured on the load line, data corrections had to be made [6].

3 RESULTS AND DISCUSION

In the case of homogeneous distribution, the hydrogen charge produced hydride precipitates of δ phase type, platelet shaped, oriented in planes parallel to the rolling direction, mainly at inter-granular sites. The distribution and size of hydrides is influenced to a great extent by the cooling rate [7]; at slow cooling rates the platelets were grouped in long bands. In the case of heterogeneous distribution, the hydrides were mainly concentrated at the crack tip; this concentration diminished in an exponential way from the tip, as can be observed in figure 1.a where this dependence was plotted for several specimens as a function of the distance from the crack tip. Figures 1.b and 1.c show two micrographs of the same specimen corresponding to a zone near the crack tip (1634 H ppm) and the bulk (173 H ppm), respectively. Hydrides precipitated generally at the grain boundaries following their curvatures, and a continuous network of hydride along the grain boundaries was often observed for the high hydrogen content zone. Within the near crack tip zone, *i. e.* the highest concentration zone, transgranular precipitation was also observed.

Throughout the analysed temperature range, fracture behaviour was always macroscopically ductile for specimens with homogeneous H distribution at several levels, being then J_{IC} the parameter characterising the fracture toughness. The J_{IC} dependency on H content at room temperature is plotted in figure 2.a, showing a high susceptibility of the toughness for small H variations at low H values, but a lower dependence for H concentrations higher than 250 ppm. This tendency was also observed at the different temperatures tested. J_{IC} values at different temperatures for the as-received H content are shown in figure 2.b. Very large blunting values at the beginning of crack growth were obtained in tests performed at 473 K, making non-valid the calculated J_{IC}; so J_Q was reported instead. The tested specimens had the maximum thickness possible from the as-received material; therefore, thicker specimens could not be machined for test, and then meet standard acceptable J_{IC} values. Although J_Q values stand out of the standards and are not considered a material property, they contribute important information about the toughness tendencies. 'Atypical' J values were obtained at about 343 K, where a relative maximum in fracture toughness was present. Initiation and curve slope values were higher than expected, figure 6. This behaviour could be due to Dynamic

Strain Ageing effect. Ramachandran, Garde [8, 9] and other authors have reported some hardening peaks in the yield stress in tensile tests of Zr at different temperatures; so this change in the tensile behaviour must undoubtedly have consequences on the toughness values.

On the other hand, all the specimens with heterogeneous H distribution tested at room temperature failed in brittle mode without stable crack propagation, and then J_C was the parameter characterising the fracture toughness. The comparison of these J_C values (under 20 kJ/m^2) to those obtained from specimens with approximately the same bulk H levels, although with homogeneous H distribution (between 50 and 110 kJ/m^2), shows that the high concentration of hydrides at the crack tip makes the fracture behaviour shift from ductile to brittle, even where the bulk H level is low and the high concentration zone is small. The J_{IC} and J_C values at different temperatures tested are plotted in figure 3 as a function of the H content far away from the crack tip (a) and near the crack tip (b). It can be observed that for those tests performed at 343K the fracture behaviour was also brittle, as was at room temperature, figure 4, although some stable crack growth occurred before the unstable fracture. Ductile fracture behaviour was found at higher temperatures.

The expression "ductile-to-brittle transition" generally refers to a change in both micro mechanisms and macroscopic behaviour. The present study showed that, for homogeneous hydrogen distribution in the volume, the macroscopic behaviour was generally ductile with stable crack growth, although a reduction on J values as temperature diminished and H increased was concomitantly observed. Only for tests at room temperature in samples with high H contents, P vs. v records showed instabilities (pop-in or full brittle fracture for H content superior to 2000 ppm). On the other hand, for the specimens with heterogeneous hydrogen distribution, brittle fracture was observed at low and medium-range temperatures, whilst ductile behaviour was present at high temperature.

It seems that the transition from ductile to brittle behaviour could be associated with the hydride array on the crack path. A high concentration of hydrides at the crack tip
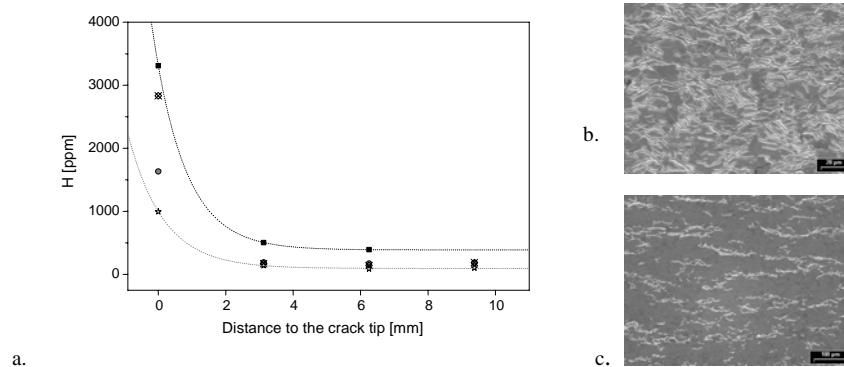

Figure 1:a- dependence on the hydrogen concentration as a function of the crack tip distance, micrograph showing the hydride distribution: b- near the, and c- far from, the crack tip.
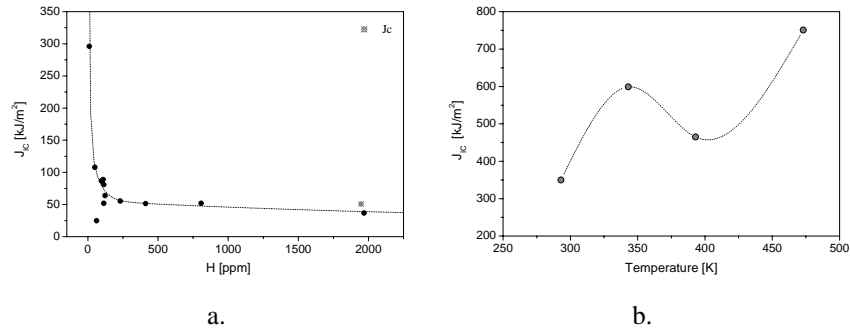
Figure 2: a- Variation of J values with the hydrogen content at room temperature and b- as a function of the temperature for a 'as-received' H level for homogeneous concentration.
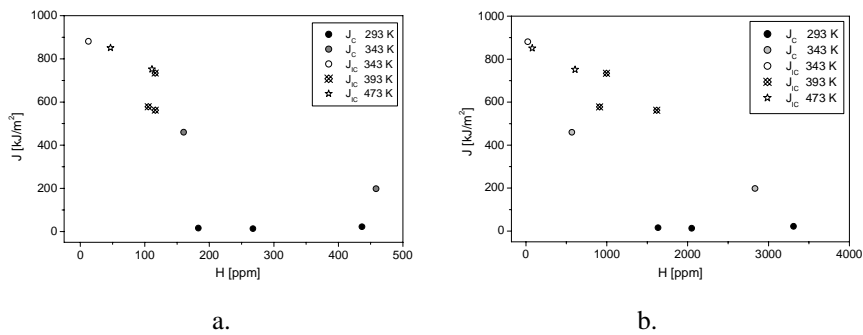

Figure 3: J values as a function of the hydrogen content for inhomogeneous concentrations a: far from the crack tip, b: near the crack tip.

leads to a high probability of finding a crack path mostly composed by hydrides (at least near the crack tip), resulting in a sudden crack growth in this region. If the matrix ductility is high enough, the unstable crack propagation can be arrested; contrarily, a fully unstable fracture is obtained.

3 CONCLUSIONS

Two different behaviours depending on the type of hydride distribution were observed.

- The main behaviour was ductile for homogeneous hydrogen distribution; only one specimen with the highest H concentration failed by brittle fracture at room temperature.
- For heterogeneous H distribution, brittle fracture was observed at room temperature without previous stable crack growth, some stable crack growth previous to the brittle fracture was observed at 324 K, and ductile fracture was obtained at the highest testing temperature.
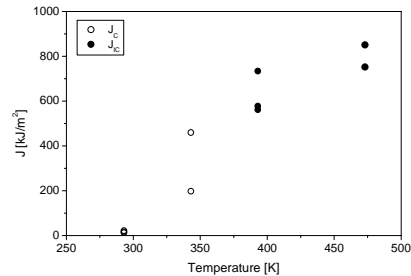
Figure 4: J values as a function of test temperature. Inhomogeneous concentration

- There were ranges in temperature and concentration where important variations in fracture toughness were measured, although there was no change in macroscopic behaviour.
- Change in the fracture mode from ductile to brittle occurred at high H concentrations (at least near the crack tip).

3 REFERENCES

[1] Vizcaíno P., Banchik A.D., Abriata J.P., Solubility of hydrogen in Zircaloy-4: irradiation induced increase and thermal recovery, Journal of Nuclear Materials, 304, pp 96-106, 2002.

[2] Ells C.E., Hydride precipitates in zirconium alloys, Journal of Nuclear Materials, 28, pp 129-151, 1968.

[3] Tenckhoff E., Deformation Mechanisms, Texture, and Anisotropy in Zirconium and Zircaloy, ASTM STP 966, 1988.

[4] ASTM E 1820-99. Standard Test Method for Measurement of Fracture Toughness. Annual Book of ASTM Standards, 03.01, pp 972-1005, 1999.

[5] D. E. McCabe, J. D. Landes, ASTM STP 803 II, 352, 1983.

[6] J.E. Perez Ipiña, Unloading Compliance method with normal precision instrumentation. Rotation corrections, Engineering Fracture Mechanics. 36-5, 797, 1990.

[7] K.W. Lee, S.I. Hong, Zirconium hydrides and their effect on the circumferential mechanical properties of Zr-Sn-Fe-Nb tubes, Journal of Alloys and Compounds. 346, 1-2, 302-307, 2002.

[8] V. Ramachandran, R.E. Reed-Hill, Metallurgical Transaction. 1, 2105, 1970.

[9] A.M. Garde, E. Aigeltinger, B.N. Woodruff, R.E. Reed-Hill, Metallurgical Transaction 6A, 1183, 1975.