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Degradation of the mechanical properties of Zircaloy-4 due to hydrogen embrittlement

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Abstract

During nuclear reactor operation, the embrittlement of components made of zirconium-based alloys is observed. The degradation of their mechanical properties is due to the combined effect of hydrogen absorption and the damage caused by neutron irradiation. In this work we studied the influence of hydrogen content on the fracture toughness of a Zircaloy-4 alloy. Compact tension (CT) specimens were obtained from a hot-rolled, annealed and finally cold-rolled material. The observed microstructure consisted of α-Zr rounded grains with diameters of about 15 μm. Selection of the tested material was guided by the need to perform experiments on samples with a texture equivalent to the cladding components of Candu-type nuclear reactors. The specimens were fatigue precracked and hydrogen charged before testing. Two different reactions were performed. Specimens with a final hydrogen content ranging from 10 to 400 ppm were obtained by electrochemical charging and those with a final concentration of up to 2000 ppm were charged by absorption under a gaseous atmosphere. In both cases, an homogeneous distribution of dissolved hydrogen and hydride phases was obtained. The dependence of the toughness on temperature and hydrogen content was measured on CT specimens. The analysis was performed in terms of *J*-integral and resistance curves.

Keywords: Zircaloy-4; Hydrogen embrittlement; Fracture testing

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1. Introduction

Much attention has recently been devoted to problems related to the degradation of the mechanical properties of zirconium alloys due to their reaction with hydrogen. The two hydride-related fracture mechanisms observed in Zircaloy cladding are radial hydride embrittlement and delayed hydride cracking (DHC).

Radial hydride embrittlement produces a reduction in fracture toughness or tensile ductility, with an increasing volumetric fraction of radial hydrides. The detrimental effects of radial hydrides in causing premature fracture of in service nuclear fuel cladding have been documented [1]. DHC involves propagation of a crack as a result of diffusion of hydrogen to the crack tip and the embrittlement of the near tip region due to hydride precipitation [2].

DHC of zirconium alloys has been recognized as a potentially important failure mechanism of high-strength pressure tubes. Recent observations in connection with long axial cracks on failed Zircaloy fuel cladding have suggested that DHC might have been the mechanism responsible for the long crack growth. The crack tip region of the long cracks was heavily hydrided with hydrides oriented perpendicular to the tensile stress [3].

In this work we present a study of the detrimental effects of the presence of hydrides at different temperatures on the fracture toughness of Zircaloy-4 (Zry-4) commercial alloy.

2. Experimental procedure

Specimens were obtained from standard hot-rolled, annealed and finally cold-rolled Zry-4. Fe, Cr, Sn and O in the proportion 0.22:0.1:1.4:0.128 wt%, respectively, in solid solution and in precipitate form were the main components present in the Zr matrix. Fig. 1 shows a scanning electron microscopy (SEM) photograph of the material microstructure. Table 1 presents values of the main mechanical properties: the ultimate tensile stress (σ_{UTS}), the yield stress (σ_y) and the elongation (ε),

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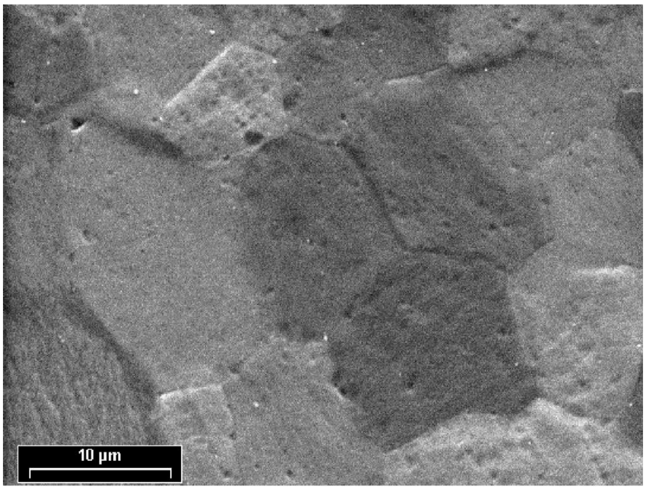


Fig. 1. SEM micrograph of the material microstructure.

measured at room temperature in the rolling direction and normal to it.

Two charging methods were used: cathodic and gaseous charging.

Cathodic charging of previously pickled samples (HF, HNO_3, lactic acid) was carried out at room temperature in 0.1 M KOH under a current of 10 mA/cm^2. After charging, the specimens were heated in an argon atmosphere for 5 h at 720 K and slowly cooled inside the furnace to room temperature.

While the above technique allows for a strictly controlled but low final hydrogen content, gaseous charging under moderate hydrogen pressure and high temperature is a useful method for obtaining a higher hydrogen concentration. The samples were placed in the reactor of volumetric equipment where they were degassed in vacuum, then heated for several hours at 720 K under a hydrogen atmosphere at a pressure of 2 bar. The samples were then slowly cooled to room temperature in the reactor. Samples with hydrogen concentrations ranging from 400 to 2000 ppm were obtained using this technique.

Although the final hydrogen content depends on the time and current for the cathodic technique and on temperature, pressure and exposure time for the gaseous method, a wide range of hydrogen concentrations was observed. Precise global concentrations were obtained using a LECO analyzer after testing and the hydride distribution of the samples was observed by SEM.

Compact tension (CT) specimens were machined to the following nominal dimensions: $W = 25.4$ mm and $B = 6$ mm. The notches were machined transversely to the rolling direction. All specimens were fatigue precracked to an a/W ratio of between 0.45 and 0.55. Specimen dimensions follow ASTM E 1820-99 [4], with $W/B = 4.23$ (outside the standard specification).

Table 1
Basic mechanical properties at room temperature

Property	Longitudinal	Transversal
σ_{UTS} (MPa)	522	510
σ_y (MPa)	365	460
ε (%)	27.8	28.6

All specimens were tested following ASTM E 1820-99, evaluating the J–R curves using the single-specimen unloading compliance technique. Specimens were fatigue postcracked after the test to delineate the crack extension. The tests were performed at 293, 343, 393, 573 and 533 K.

McCabe and Landes [5] suggested that it is not always necessary to heat the entire specimen plus the grip assembly, and were able to achieve good temperature control by heating only the zone near the crack tip with strip heaters. This technique was employed in this study using two strip heaters and measuring and controlling the temperature by means of a thermocouple welded to both specimen sides close to the crack tip.

The initiation value (J_{IC}) and the J–R curve slope for 1 mm of stable crack growth ($\varphi_{1\ mm}$) were calculated when possible. For the few specimens exhibiting brittle fracture, J_C was evaluated.

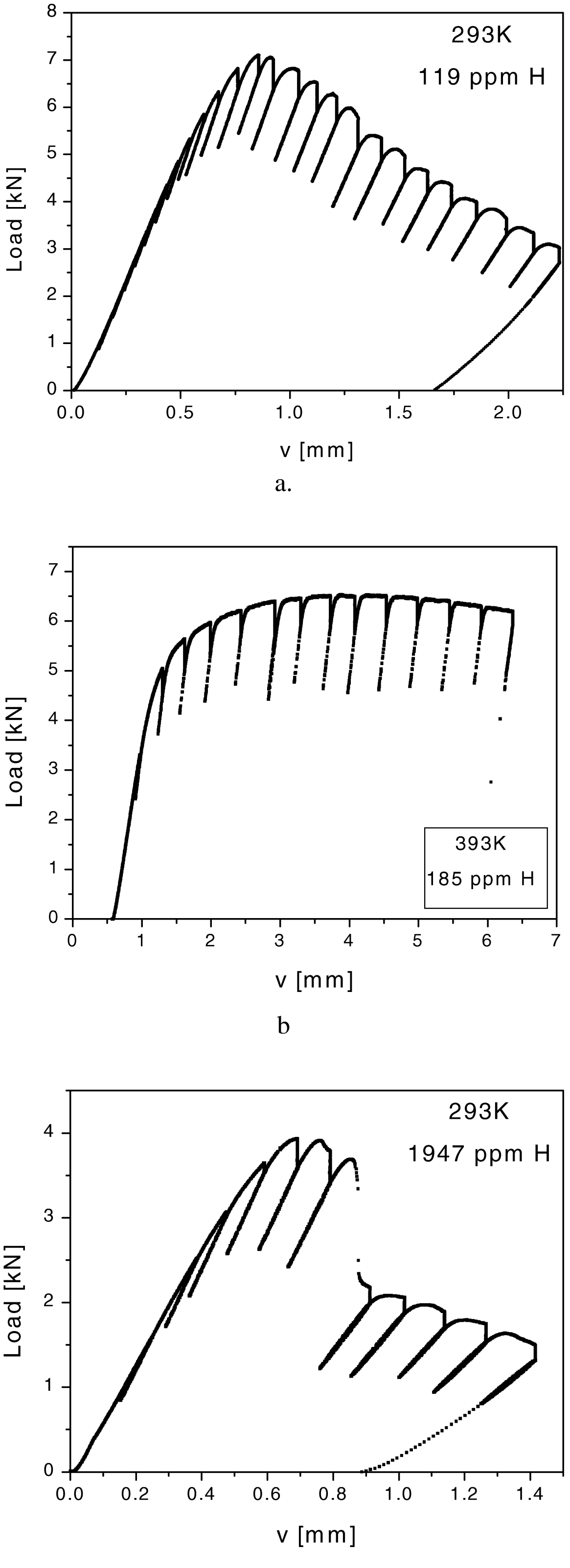
3. Results

Fig. 2 shows load–displacement records in which typical ductile behavior can be observed. Some specimens tested at room temperature (RT) exhibited sudden load drops and consequent changes in the unloading slopes (Fig. 2c). Only one specimen failed by brittle mode at room temperature.

J–R curves for different hydrogen contents and temperatures are shown in Fig. 3. A few specimens showed negative crack growth in the blunting line zone, thus hindering data analysis. This is a well-known problem, especially when the W/B ratio is greater than 2. A correction proposed in the literature [6], which consists of a zero shift of Δa, was used to overcome this difficulty. Because the compliances were not measured in the load line, corrections had to be made [7].

Fig. 4a and b show the measured values of J_{IC} and $\varphi_{1\ mm}$ for samples with hydrogen concentrations across the entire range. Fig. 4c and d present the J_{IC} and $\varphi_{1\ mm}$ dependence with respect to concentration at room temperature.

The fracture surface shown in Fig. 5 corresponds to a specimen charged with 400 ppm of hydrogen and tested at 293 K. It presents a ductile fracture with dimples associated with ductile metallic ligaments. Fig. 6 shows the fracture surface observed in a specimen that fractured in brittle mode. Large longitudinally oriented cracks can be observed. Fig. 7 shows that the platelets of hydride phase were transversely oriented, normal in the rolling direction and homogeneously distributed over the entire surface of the specimen.

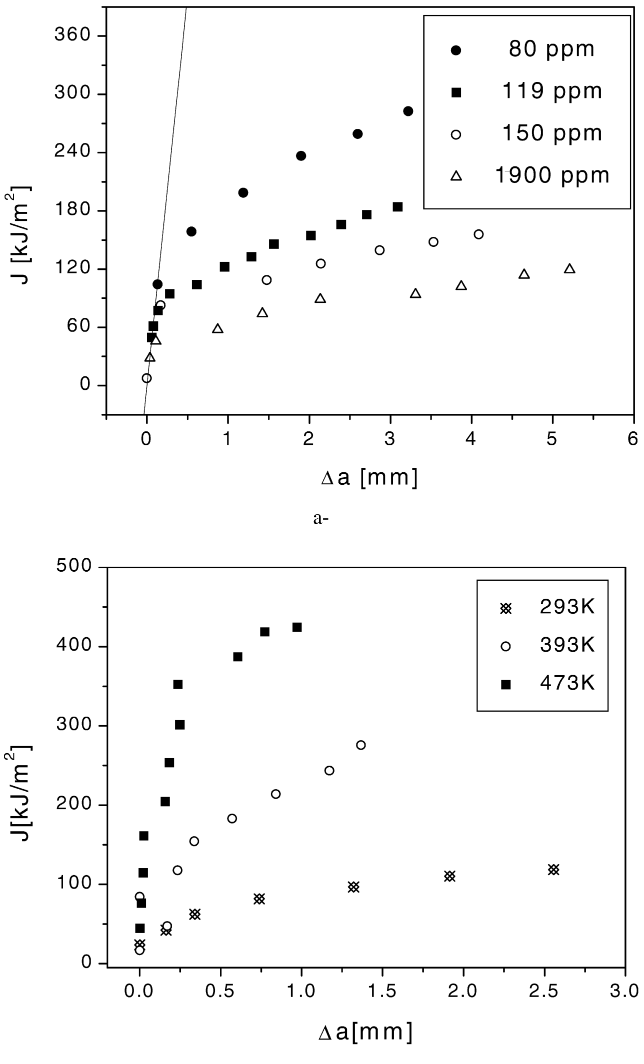


a.

b

c.

Fig. 2. Load–displacement records obtained for specimens with different hydrogen content at: (a) 293 K, (b) 393 K, (c) 293 K.



a-

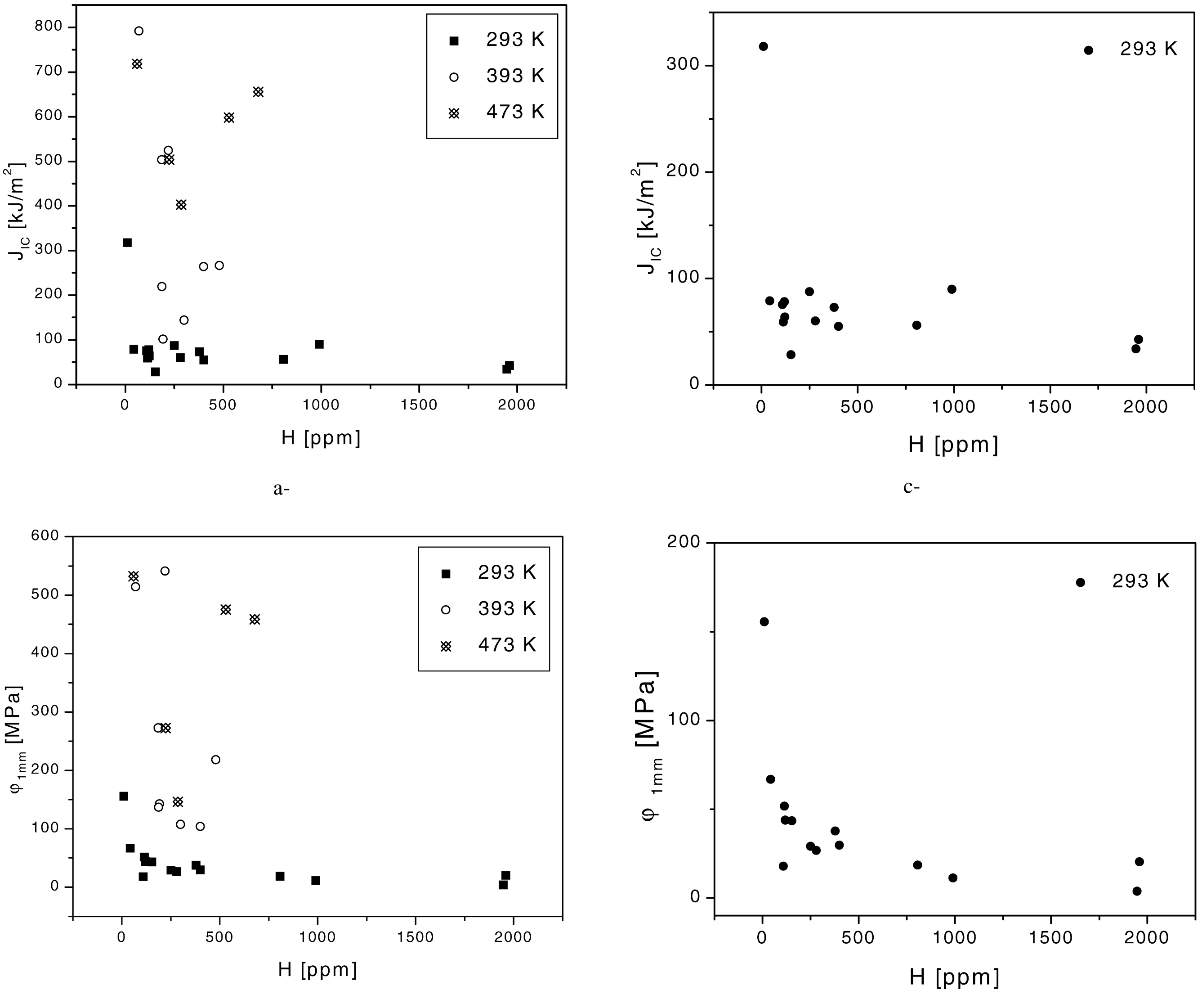
b-

Fig. 3. *J*–*R* curves for (a) different hydrogen contents at 293 K, (b) different temperatures for 200 ppm H content.

4. Discussion

The terminal solid solubility of hydrogen in Zircaloy-4 increases from 0.01 to 10 wt ppm over the temperature range 293 to 473 K [8,9]. Thus, most of the samples studied were located in the two-phase region of the equilibrium phase diagram during the tests, which means that hydride platelets were nucleated from the grain boundaries into the Zr matrix. Although the influence of second-phase precipitates and their hydrides on the mechanical properties of Zircaloy is not completely understood, Zr-hydride precipitates clearly reduce the ductility of Zircaloy deformed over the temperature range 293 to 616 K [3].

As a consequence of the obtained load–displacement records, including the tests resulting in brittle fracture, elastic plastic fracture mechanics were considered an



a-

c-

b-

d-

Fig. 4. (a) J_{IC} and (b) $\varphi_{1\ mm}$ dependence on temperature and hydrogen content; (c) variation of J_{IC} and (d) φ_{IC} with hydrogen content at RT.

adequate methodology for analyzing hydrogen embrittlement over the concentration and temperature ranges studied.

Although the experimental data varied, it is clear that the J-integral values diminish when the hydrogen concentration increases according to the considerations presented above. In the tests performed at 473 K, very high J-integral values were obtained and calculated J_{IC} results were invalid, thus only J_q values were reported. Thicker probes will have to be machined in order to obtain more useful values. J–R curves could not be obtained because the blunting process was too large (Fig. 8) and no stable crack growth was present during the tests.

Toughness values clearly tended to decrease as the temperature was lowered, however the fracture behavior was nearly always macroscopically ductile. Only at room temperature and at high hydrogen concentrations did some specimens fail in brittle mode. As compared to steels, where the expression 'ductile-to-brittle transition' refers to a change in both the mechanisms and the macroscopic l–d behavior, there were important differences in the behavior of Zry-4 over the temperature and hydrogen concentration ranges studied. It would be interesting to determine whether the ductile-to-brittle transition is applicable to this case since the decrease in toughness was not always accomplished by a change in the macroscopic l–d mode.

The fractographic observations clearly show the influence of the hydride precipitate in the fracture path. The hydride precipitates mostly lie parallel to the rolling direction.

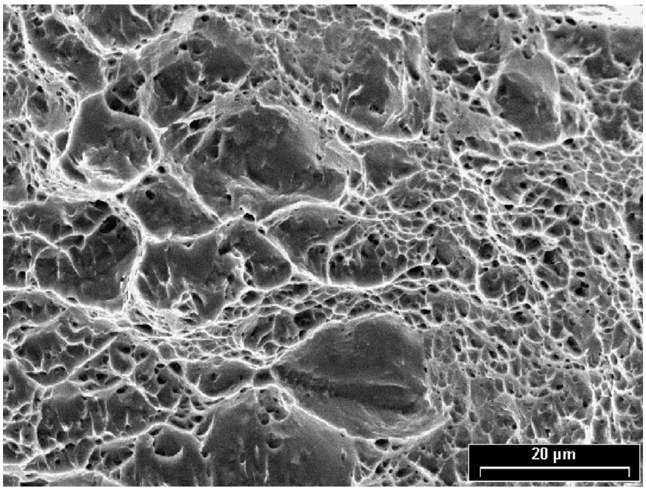
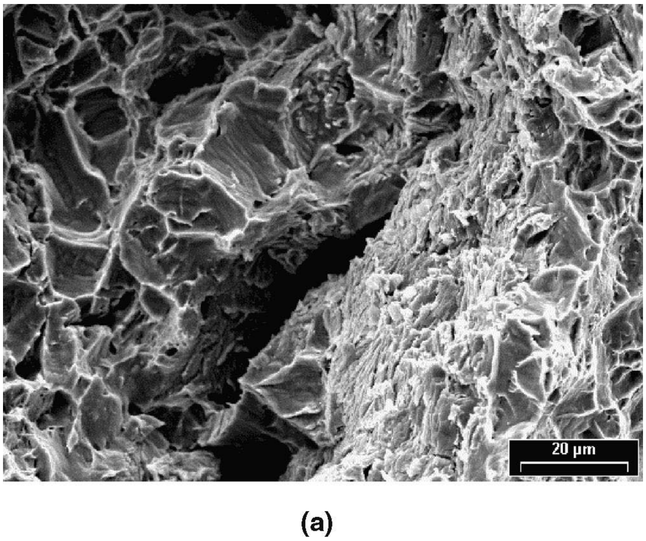


Fig. 5. Fracture surface corresponding to a specimen charged with 400 ppm of hydrogen and tested at 293 K. It presents a ductile fracture with dimples associated with ductile metallic ligaments.



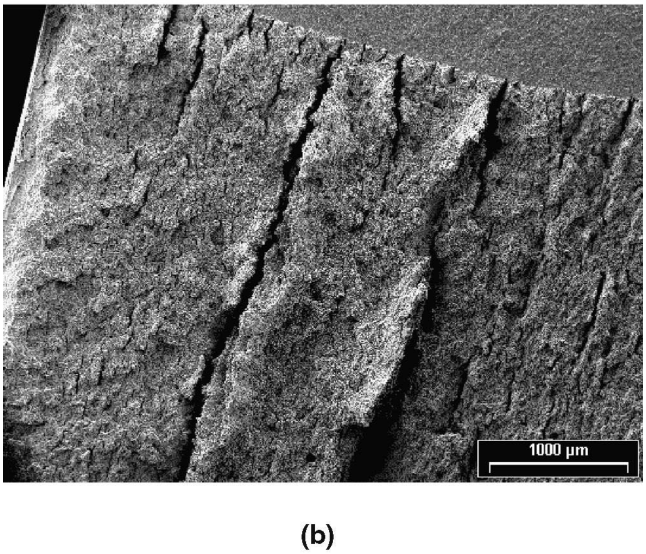


Fig. 6. (a) Fracture surface observed in a specimen that fractured by brittle mode. (b) Large longitudinally oriented cracks.

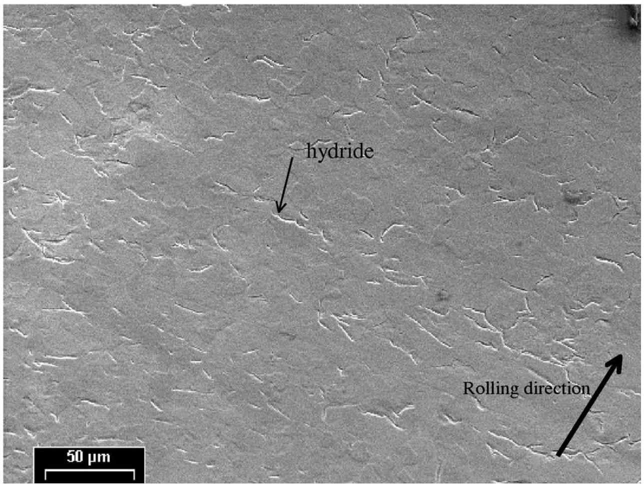


Fig. 7. Platelets of hydride phase, oriented normal to the rolling direction and with a homogeneous distribution over the entire surface of the specimen.

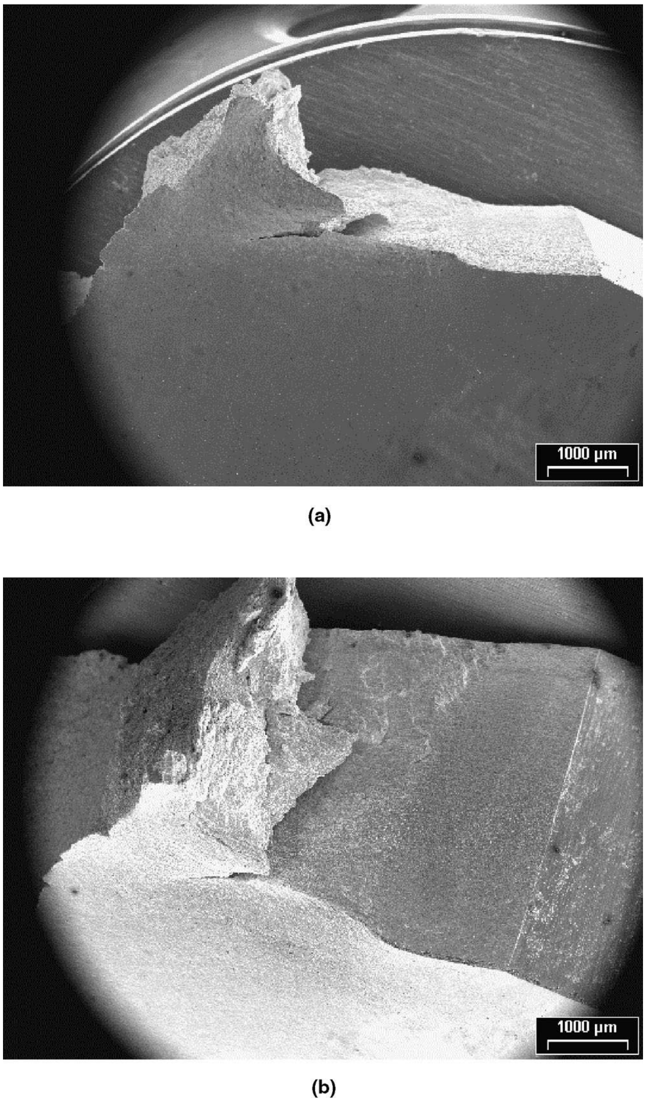


Fig. 8. SEM photographs of the blunting zone of a specimen tested at 473 K.

5. Conclusions

In this work we present a study of the hydrogen embrittlement of CT-type probes of Zry-4 in the temperature range from RT to 533 K and hydrogen content from 10 to 2000 ppm.

Except for some specimens at room temperature, the fracture mode was always ductile over the range of temperatures tested.

Both J_{IC} and the slope of the J–R curves increased as the H content diminished or the test temperature increased.

At high temperature and low H content, some specimens showed a very high initiation toughness, which did not allow J–R curves to be obtained.

The expression 'ductile-to-brittle transition' seems to be inadequate to describe the toughness decrease in Zry-4 within the hydrogen contents and temperature ranges used.

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