The detailed microscopic processes of hydrogen embrittlement in Zircaloy-4(Zy-4) tested at room temperature have been examined using in situ SEM studies, fractography and fracture profile observations. The fracture surfaces are characterized by voids and secondary cracks for low and medium hydrogen contents (C_H), and by intergranular crack and decohesion through the continuous hydride network for high C_H. Metallography observations below the fracture surface reveal that for Zy-4 containing low or medium hydrogen contents, a realignment of the hydrides occurs during straining. Only the voids originating in the perpendicular cracked hydrides contribute to the fracture process. Tensile tests on specimens with oriented hydrides have shown that these hydrides cause a large reduction in ductility earlier in the process. There is little variation in the onset of fracture initiation at hydrides as a function of hydrogen content. Regardless of the different hydride morphologies for the stress-relieved and recrystallized states, hydride fracture initiates after only a small amount of macroscopic plastic deformation, about 2-3% and occurs continuously throughout the plastic deformation stage.

INTRODUCTION

Hydrogen is readily absorbed into zirconium alloys during service in high temperature water environments. When hydrogen concentration exceeds the terminal solid solubility, the excess hydrogen precipitates as zirconium hydrides (ZrH_2) which result in a severe ductility degradation. Various efforts have been made to determine a criterion for the fracture of individual hydride platelets [1-4]. In a recent work, tensile specimens were used to study the initiation of fracture at hydride platelets as a function of stress, stress state, hydride platelet length, and matrix strength [4]. Consequently, the present study emphasizes the comparison between the fracture initiation behaviors at hydrides in Zy-4 containing hydrogen concentration up to 1400 ppm of different metallurgical states. In situ SEM studies, SEM fractography and fracture profile observations were carried out to examine the detailed microscopic processes which occur during the hydrogen embrittlement of Zy-4 tested at room temperature.

EXPERIMENTAL

Material and Tensile Test. The specimens were made of 0.5 mm thick Zy-4 cold-rolled (38%) sheets in stress-relieved (460°C, 24 hours) and recrystallized (650°C, 3 hours) states [3]. The chemical analysis and smooth tensile specimen geometry are shown in Table 1 and Fig. 1, respectively. The tensile tests were carried out at room temperature (20°C) on a screw-driven Instron machine. The specimens were loaded at an engineering strain rate of 4x10^{-4}/s.

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Hydriding Procedure. Specimens with the tensile axis along the transverse direction of the cold-rolled sheet were gaseously hydrided at 400°C for different durations, and cooled down to room temperature with a cooling rate < 1.4°C/min. Hydriding under tensile stress was also carried out to obtain the hydride orientation mainly perpendicular to the tensile axis. For each specimen, after tensile testing, offset near the fracture surface was taken for hydrogen content analysis at 850°C, using a vacuum desorption technique.

Hydride Morphology Study. The hydride morphology is a complex function of stress effects and microstructure (texture, grain size and shape) and has a significant influence on the mechanical behavior of Zry-4. In our study, the hydride morphology is quite different in the two metallurgical states. For the stress-relieved state, hydrides are aligned in the cold-rolled plane up to about 600 ppm wt H, then begin to exhibit some random distribution, with platelets having an in-plane size of about 15-20 μm; for the recrystallized sheet, there is a more random distribution of hydrides, having a size determined by the grain boundary characteristics with platelets size of about 7 μm. Hydride thicknesses determined by transmission electronic microscope vary between 0.1 and 1.0 μm.

RESULTS

Tensile Test Results. It is found generally that the effect of increasing hydrogen concentration on strength is not important. However, at room temperature there is a ductile-brittle transition when the hydrogen concentration is higher than a certain threshold, as shown in Figure 2.

Fractography and Fracture Profile Analyses. The fracture surfaces are characterized by voids and secondary cracks for low and medium hydrogen contents, and by intergranular cracks and decohesion through the continuous hydride network for high hydrogen contents. Metallography observations below the fracture surface reveal that for Zry-4 containing low or medium hydrogen contents, a realignment of the hydrides occurs during straining. Along these hydrides some fragmentation appears, with fractures distributed more or less randomly along their length. Only the voids originating in the cracked hydrides perpendicular to the tensile axis
contribute to the fracture process. Tensile tests on specimens with oriented hydrides show that these hydrides cause large reduction in ductility for smaller hydride volume fractions. There is little variation in the onset of fracture initiation at hydrides as a function of hydrogen content.

**In Situ Tensile Tests.** In situ tensile test on hydrided specimens were carried out inside a SEM. The specimens were strained slowly and the surface morphology evolutions were recorded simultaneously. The force vs displacement curves recorded during the test are shown in Figure 3, with a and b being the stress-relieved specimens and c being the recrystallized specimen. It was observed that for the specimens containing low and medium hydrogen concentrations the first cavities due to the hydrides appear at grain boundary triple nodes for the recrystallized state (Collage 1.1) and at hydride tips for the stress-relieved state (Collage 1.2). The small hydrides do not have an important influence on the fracture process, because they can rotate with the grain to accommodate the plastic deformation in the matrix. Numerous spherical cavities form in the necked region of the tensile specimens but these small and isolated cavities often keep their initial size and have no influence on the tensile properties of Zy-4. For a highly hydrided stress-relieved specimen, the surface appearance is quite different. Small cracks appear instead of cavities perpendicular to the stress. The coalescence of these cracks results in the final brittle fracture (Collage 1.3). Regardless of the different hydride morphologies for the stress-relieved and recrystallized states, hydride fracture initiates after only a small amount of macroscopic plastic deformation, about 2-3% and occurs continuously throughout the plastic deformation stage.

**Test with Stress Oriented Hydrides.** Tensile tests were also carried out on the specimens hydrided under tensile stress which produces hydrides perpendicular to the stress ([5,5]). This kind of hydrides results in a faceted fracture surface. The size of these facets is the same as those of the hydrides. An alignment of the hydrides crossing the specimen section can induce a completely brittle fracture at much lower hydrogen content. Figure 4 shows two tensile test curves of specimens with oriented or non-oriented hydrides. Obviously, the oriented hydrides are much more noxious and should be avoided or minimized by controlling the residual stress, texture and microstructure [5].

**DISCUSSION**

**Ductile Fracture.** The ductile fracture of hydrided Zy-4 occurs by the formation and subsequent growth and coalescence of voids. The controlling stage appears to be the failure of the matrix connecting the cracked hydrides. Therefore, in Zy-4 containing low or medium hydrogen, the difference of mechanical properties between the stress-relieved and recrystallized states can be explained by the different hydride morphology. In the former, the hydrides are aligned in the stress direction and the small cavities which form at the hydride tips do not affect the ductility. For the recrystallized state, the hydrides distribute randomly with some intrinsic percentage of hydrides perpendicular to the stress direction. The number of cracked hydrides increases continuously as a function of hydrogen content for all tests, thus inducing a progressive ductility reduction. From the metallography observations, we can draw the same conclusion as Puls did that different hydrides or different parts of the same hydride, can have significantly different susceptibilities to fracture. The reasons for this could be due to differences in the hydrides lengths, shapes, orientations, and locations in the grains, all factors that could be readily determined using standard metallographic techniques. However, the different cracking
susceptibilities of the hydrides could also be due to variations in imperfections in the structures of the hydrides, a factor that is not so easily determined by standard analytical techniques or predetermined by controlling the methods of specimen preparation [1].

Figure 5 shows a fracture micromechanism table for hydrided Zy-4 during tensile tests. For the two states, the formation of a continuous hydride network completely embrittles the specimens because the tensile properties of the specimens are controlled by the brittle hydride characteristics. The transition is more spread out for the stress-relieved state than for the recrystallized state owing to the lower increase rate of the perpendicular hydrides percentage demonstrated by the hydride morphology study. The fine microstructure and favorable grain boundary orientation result in a high hydrogen content at the ductile-brittle transition for the stress-relieved state.

<table>
<thead>
<tr>
<th>Ductile fracture</th>
<th>Transition</th>
<th>Brittle fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discontinuous hydride network</td>
<td>1. Nucleation of cavities at hydride tips, hydride fragmentation</td>
<td>Fracture following continuous hydride network</td>
</tr>
<tr>
<td>Cracked-hydride voids coalescence</td>
<td>2. Triple nodes or cracked perpendicular hydrides, hydride fragmentation</td>
<td>High C/H</td>
</tr>
<tr>
<td>Ductility reduces with increasing void density (hydrogen content)</td>
<td>Low and medium C/H</td>
<td></td>
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</tbody>
</table>

Figure 5 - Fracture micromechanism table for hydrided Zy-4 at 20°C.

Fracture Initiation. In this section, we will analyze the mechanical condition for fracture initiation at hydrides. Several studies have clearly established that deformation causes hydride fracture and, in most instances, subsequent void
nucleation along the fracture in the hydride platelet [3,6]. Among the current existing criteria for damage initiation, the most appropriate ones for the present case are two models: Tanaka and Mori's model in terms of surface energy [7] and Beremin's in terms of critical stress [8]. The first, however, gives the same critical plastic deformation of decohesion in the matrix for any hydride orientation. The second shows that the parallel hydrides crack before the perpendicular ones assuming that they have the same fracture criterion. These results are contrary to the experimental observations [1,3]. In the two directly related papers, the authors stated that hydride size did not appear to be an important factor in the failure mechanism [1,2]. This could be true for the hydrides parallel to the stress axis. For the perpendicular hydrides, however, the larger ones were cracked earlier than the smaller ones. Bourcier and Koss's analysis indicated that the effectiveness of plane strain and equibiaxial deformation in fracturing hydrides could be understood on the basis of the hydrides failing at a critical value of the maximum normal stress within the hydride [9]. These normal stresses depend strongly on the inhomogeneity of strain between matrix and hydride. On the other hand, the precipitation of hydrides induces residual stresses around the hydrides and influences the fracture initiation at hydride. Some special efforts have been devoted to estimate these stresses. The present author suggests a macroscopic deformation model which defines the mechanical condition for fracture initiation at hydrides. Thus, the deformation in the matrix should be large enough to allow to overcome this local residual compression first and then to make the stress reach the fracture stress of hydride. This model enables to take into account the anisotropic feature of fracture initiation as a function of hydride orientation by considering local mechanical state. The idea of our model is confirmed by Puls's work [1]. He has found that the hydrides in a softer matrix (yield stress < 300 MPa) can fracture under externally applied stresses that are much smaller than those needed when the hydrides are situated in a harder matrix material. The reason for this is that the misfit-induced compressive stresses would decrease with a decrease in the yield stress of the matrix. The mechanical calculation shows that the critical deformation values are 2.9% for the stress-relieved state and 2.2% for the recrystallized state assuming that Zry-4 has a very low hardening rate [3]. Another indirect verification is that the onset of hydride cracking is lower or near the proportional limit for the oriented hydrides. Probably the compressive stresses around these hydrides are very low because the hydriding was carried out under tensile stress.

CONCLUSION

Metallography reveals that for Zry-4 containing low or medium hydrogen contents, a realignment of the hydrides occurs during straining. Along these hydrides some fragmentation appears. Only the voids originating in the cracked hydrides perpendicular to the tensile axis contribute to the fracture process. The oriented hydrides cause a large reduction in ductility. Regardless of the different hydride morphologies for the stress-relieved and recrystallized states, hydride fracture initiates after only a small amount of macroscopic plastic deformation, about 2-3% and occurs continuously throughout the plastic deformation stage.

REFERENCES


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Collage 1.1: recrystallized state, 275 ppm H, cavities at grain boundaries, triple nodes and voids due to perpendicular hydrides.

Collage 1.2: stress-relieved state, 419 ppm H, cavities at hydride trips.

Collage 1.3: stress-relieved state, 1400 ppm H, perpendicular cracks.