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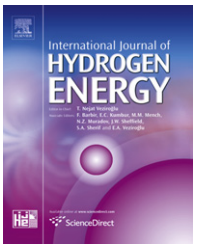

Hydrogen absorption cracking of zirconium alloy in the application of nuclear industry

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ABSTRACT

The hydrogen absorption cracking behavior of Zr-4 has been investigated based on the microstructure, hydrogen absorption amount as well as residual stress. The results show that the grain size has a pronounced effect on the hydrogen absorption cracking, with the increase of grain size from 30 μm to 500 μm, the cracks vary from small cracks of independence to large cracks that connect with each other along the radial direction. The unsaturated hydrogen absorption samples which consist of γ- and δ-hydrides present a crack-free surface while the saturated hydrogen absorption samples which consist of ε-hydride exhibit not only large cracks but also bulges on the surface. The hydride decomposition temperatures of ε → δ and δ → α during dehydriding are determined to be about 600 °C and 700 °C respectively. In the unsaturated hydrogen absorption samples, both the thickness expansion and radial residual stress present a positive liner correlation with the hydrogen absorption amount. Based on the experimental results a mechanism of hydrogen absorption cracking is proposed in zirconium alloys.

1. Introduction

Zirconium alloys are kinds of materials of great importance in the nuclear industry owing to its good mechanical properties, low absorption cross-section for thermal neutrons and excellent corrosion resistance in high temperature water [1,2]. Currently, zirconium alloys are used not only as structural materials of fuel cladding in water cooled reactors, but also as fuel core materials, such as fuel moderator and laser-fusion fuel target, in nuclear fission and fusion reactors. In the application as structural materials, it works under the circumstance of water cooled systems. Hydrogen produced by the corrosion reaction between zirconium and water will be absorbed by zirconium alloys which results in the formation of zirconium hydrides [3–6]. These hydrides lead to the dilatational strain and cause the alloy to crack when the hydrogen content exceeds its critical values. Delayed hydride cracking (DHC) is one of the cracking mechanisms of great importance in analyzing the failure of zirconium alloys. It involves stress-induced hydrogen diffusion, hydride precipitation and growth, as well as subsequent fracture [7–9]. In the investigation concerning DHC, however, it is only available with low hydrogen concentration, which is less than 2000 ppm. With the hydrogen concentration increasing to a higher level, when occasionally the coolant water decomposes and produces a great deal of hydrogen at elevated temperature, little has been known on the behavior of hydrogen absorption cracking. Thus, it is necessary to investigate the response of zirconium alloys in the high hydrogen concentration circumstance.

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Besides, as has mentioned above, zirconium hydrides can also be used as core materials on the occasion of fuel moderator and laser-fusion fuel target [10]. When charged with hydrogen, the transformation from zirconium to zirconium hydrides will bring about lots of cracks in zirconium matrix due to the precipitate of the brittle zirconium hydrides [11]. This makes it difficult to prepare zirconium hydrides in a bulky form. Thus, how to reduce the cracks so as to obtain bulky zirconium hydrides is a critical issue in the application of zirconium hydrides.

Three types of zirconium hydrides have been identified, namely γ-hydride ($ZrH_{1.0}$, tetragonal, c/a > 1), δ-hydride ($ZrH_{1.5-1.66}$, face-centered cubic) and ε-hydride ($ZrH_{1.8-2}$, tetragonal, c/a < 1) [12,13]. The precipitates of γ-, δ- and ε-hydrides which result in a misfit strain are believed to be the main reasons to crack [12,14,15]. Some literatures reported that the volume expansions were 12.3% and 17.2% per unit cell respectively in the phase transformation of $\alpha \rightarrow \gamma$ and $\alpha \rightarrow \delta$ [16,17]. But detailed mechanisms and influencing factors that control the cracking still lack of understanding, especially at a high hydrogen concentration.

In this paper, hydrogen absorption samples of zirconium alloys with high hydrogen concentration were prepared using a Sievert's device. The effects of microstructure, hydrogen absorption amount, hydride types, residual stress, hydrogen absorption/desorption process on the cracking are discussed. A mechanism of hydrogen absorption cracking in zirconium alloys is proposed based on the experimental results and some factors that minimize the cracking have been suggested.

2. Experimental details

2.1. Materials

Zircaloy-4 alloys were used in this study. The nominal composition of Zircaloy-4 is Sn: 1.20–1.70 wt.%; Fe: 0.18–0.24 wt.%; Cr: 0.07–0.13 wt.%; Zr and impurities to balance. The disk samples were cut by an electron discharge machine from the as-received Zircaloy-4 rod to the dimension of φ 8 × 1 mm with a hole of φ 2 mm in the center. After polished down to 1200 grit with SiC paper, samples were heat treated at 750 °C/FC, 950 °C/FC and 950 °C/WQ separately in vacuum to obtain different microstructures.

2.2. Hydrogenation

Hydrogen absorption experiments were carried out by a gaseous charge method using a Sievert's device, which is an apparatus widely used in the determination of the hydrogen absorption and desorption kinetics, hydrogen absorption capacity as well as the pressure–composition (P–C) diagram of the material–hydrogen system by measuring the pressure variation in a leaktight chamber. The samples were heated to 700 °C in a vacuum chamber and then the highly purified hydrogen was charged into the chamber for hydrogen activation and absorption. The hydrogen activation process took about ten minutes and then the hydrogen absorption process lasted for four hours. After hydrogen absorption, the chamber was cooled down slowly in the hydrogen atmosphere. Hydrogen absorption amount was controlled by the variation of hydrogen pressure, and was calculated based on the ideal gas equation $\Delta PV = \Delta nRT$, among which Δn is the amount of hydrogen absorption, ΔP is the variation of pressure, R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature of samples inside the chamber. The deflection of temperature during test was within the accuracy of ±1 °C. Note that the samples were still in hydrogen atmosphere during cooling and would absorb hydrogen further, so the hydrogen absorption amount determined by pressure variation would be further calibrated based on the measurement of weight gain after hydrogenation. For the hydrogen desorption process, the samples were heated to the temperature of 700 °C again in the chamber with a vacuum degree of 10^{-1} Pa for hydrogen release.

2.3. Phase structures

The phase structures of the samples before and after hydrogen absorption were identified by a Rigaku TTRIII X-ray diffractometer (XRD) using Cu K_α-radiation. The morphology and types of zirconium hydrides, which are γ-, δ- and ε-hydride respectively, were examined by transmission electron microscope (TEM). The decomposition of zirconium hydrides with the temperature was also determined by an *in-situ* X-ray diffraction in the temperature range of 100 °C–800 °C.

2.4. Observation of cracks and determination of residual stress

The macro cracks on the surface of samples were observed using a low magnification (×5) optical microscope (OP). The expansion after hydrogen absorption was determined by the measurement of thickness variation. Residual stresses in radial and circular directions were examined using an X-350A stress analyzer with the 2θ range of 120–170° and ψ of 0–60°.

3. Results and discussion

3.1. Influence of microstructure on cracking

The microstructures of Zircaloy-4 before and after heat treatment are illustrated in Fig. 1. Four types of microstructures are obtained, namely original rolling, annealing, furnace cooling and water quenched microstructures. The rolling sample shows a fine grain structure with a large amount of grain boundaries distributed along the as-rolled orientation. The annealing sample exhibits an equi-axed and recrystallized grain with the grain size of about 30 μm. The furnace cooling sample is a basket weave structure with packets of α phase precipitated from the coarse grain boundaries. The grain size is nearly 500 μm. The water quenched sample presents a coarse microstructure of more than 500 μm in grain size, with a few α-phase plates distributed inside the grains.

The macrographs showing cracks of different microstructures after hydriding are illustrated in Fig. 2(a). It can be seen that the rolling sample shows the minimum cracking tendency with small cracks and flat surface, while the quenched sample shows the maximum cracking tendency with large

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