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Study of the microstructure evolution of zirconium alloy during deuterium absorption at high temperature

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ABSTRACT

In the exploration of fusion power, zirconium alloy has been viewed as a potential deuterium storage material to store and deliver deuterium fuel into fusion reactors, due to its large deuterium storage capacity, low deuterium desorption pressure and fast deuterium absorption kinetics. But it often cracks after deuterium absorption. In this study, the microstructure and deuterium absorption kinetic of β-Zr in various deuteriding conditions (pressure, time and temperature) were investigated. The results showed that, with the increase of deuteriding pressures from 1 bar to 3 bar at 1173 K, the deuteride content and the deuteride morphology changed significantly. During deuterium absorption at 3 bar, the surface deuteride layer was formed first, and then the inner deuteride network was gradually developed with the time. There existed an apparent deuterium concentration gradient from surface to center. With the increase of deuteriding temperatures from 973 K to 1173 K, the deuteride content decreased. The kinetic of deuterium absorption at 1173 K was found to be affected by the deuteriding pressures. Transmission electron microscopy (TEM) results showed that ε deuterides nucleated and grew at the interface of δ deuterides, and small bands with different crystal orientation were found within the ε deuterides. The γ deuterides were found at 3 bar, within which twins and tweed structure were observed. An orientation relationship of $\langle 011\rangle_{\delta}//\langle 011\rangle_{\varepsilon}$, $\{111\}_{\delta}//\{111\}_{\varepsilon}$ between δ and ε deuterides was also determined by TEM analysis.

1. Introduction

With the unprecedented growth of worldwide demand for energy, nuclear power has come to be considered as a reliable, affordable and sustainable source of energy to replace fossil fuel [1]. Fifty years ago, nuclear fission reactor emerged and has made a great contribution to the supply of power and the reduction of carbon emissions. However, there has always been public concern about the safety of fission reactors, in particular the danger of nuclear leaks and the difficulty of safely storing nuclear waste. In contrast to fission reactors, fusion reactors, which display higher energy output and better safety, have come to attract more and more attention. Due to the rigorous reaction conditions, the fusion reactor can be automatically terminated in case of an accident. And its products contain no radioactive hazard. But how to make it widely available is one of the greatest challenges that scientists face today.

We know that huge energy is released by the combination of deuterium (D) and tritium (T), $^{2}D+^{3}T\rightarrow^{4}He + n+17.6$ MeV. Experimental fusion reactors, such as the National Ignition Facility (NIF) and the International Tokamak Experimental Reactor (ITER), have been or are being built, and the exploration of the key issues is now underway [2,3]. One of these crucial issues, as yet unresolved, is how to store and deliver deuterium with large capacity and high safety [4,5]. Currently, deuterium is stored in a uranium bed. After deuterium absorption, the uranium suffers severe pulverization, which causes the degradation of its deuterium absorption/desorption properties [6,7]. The pulverization of the uranium also increases the possibility of pyrophoricity [8], which is a potential danger for the reactor. Moreover, uranium itself is rare and expensive for the storage of deuterium. Hence it is necessary to discover an alternative material to replace uranium for deuterium storage.

Zirconium and its alloys have been reported to have favorable deuterium storage properties with large capacity, low deuteride decomposition pressure at room temperature and fast deuterium

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release rate at elevated temperatures [9–11]. Also, zirconium has less volume expansion (17.2% [12]) than uranium (70% [7]) after deuterium absorption. Thus, zirconium is a promising candidate for the storage and delivery of deuterium. However, it has been reported that cracking has occurred in zirconium alloys after hydrogen absorption [13–16]. Studies have shown that the cracking was closely related to the hydriding microstructure, which included with hydride types [15,17], morphology [18,19] and distribution [20–22]. But information about the microstructure evolution of zirconium alloy during hydrogen absorption is very limited, which in turn limits the understanding of cracking of zirconium alloys as deuterium storage materials.

There are four types of hydride (ζ, γ, δ and ε) which have been identified in Zr-H system. The crystallography of these hydrides has been reviewed in the literature [23–25]. Among them, δ and ε hydrides are normally reported as stable phases in zirconium alloy, while the other two phases are reported to be unstable [25,26]. The δ hydride is commonly observed to be plate-shaped when viewed through an optical microscope. It is always consist of stacks of smaller δ hydride platelets, as has been observed by TEM [27]. The ε hydride has a higher hydrogen content, and has a “herringbone” morphology composed of small twins [28]. It has been shown that the ε hydride has a lower fracture toughness than the δ hydride [29], and the formation of the ε hydride leads to a larger volume expansion and severe cracking [13]. For the γ hydride, it has been reported that its stability is affected by the cooling rate [30], temperature [31] and matrix microstructure [32].

The precipitation of the hydrides depends highly on the microstructure of the zirconium alloy. Both intragranular and intergranular hydrides have been observed after hydrogen absorption [33]. Studies have shown that the nucleation of intragranular hydrides needs more energy to overcome large lattice misfit [12] and volume expansion [34]. Thus intergranular hydrides become much easier to precipitate than intragranular hydrides. Furthermore, the work of Qin et al. [20] has shown that the precipitation of intergranular hydrides is governed by a combined effect of grain boundary and matrix orientation. And the precipitation of massive intergranular hydrides, which leads to the formation of an inter-linked hydride network when the hydrogen content reaches a certain level, causes a ductile-brittle transition in zirconium alloy [35–38].

The studies mentioned above focus on the hydrides formed in α-Zr, at a temperature which is usually lower than the eutectoid temperature (823 K in Zr-H system [39]). But for β-Zr, which appears at a temperature higher than 823 K, has larger deuterium solubility [40] and a higher tolerance of cracking after deuterium absorption [14]. Studies have shown that β-Zr promotes the precipitation of intergranular hydrides [41] and affects the kinetic mechanism of hydrogen absorption [42]. It has also been reported that the presence of β-Zr promotes the precipitation of γ hydride [43,44]. However, there has been less systematical discussion as yet of the microstructure evolution in β-Zr during deuterium absorption.

In this study we aim to understand the microstructure evolution in β-Zr alloy during deuterium absorption. The effects of pressure, time and temperature on the deuteride distribution, phase structure, and absorption kinetic in β-Zr are investigated.

2. Experimental

2.1. Materials

The composition of as-received Zircaloy-4 alloy is listed in Table 1. The as-received Zr-4 alloy was annealed at 1073 K for 5 h in vacuum to obtain the equiaxed α-Zr, and was sectioned to samples with a dimension of 4 × 4 × 8 mm for deuterium absorption.

2.2. Deuterium absorption

Deuterium absorption was carried out in a Sievert's apparatus using high purity deuterium (99.999%). The deuteriding temperatures were 973 K, 1073 K and 1173 K, and the deuteriding pressures were 1 bar, 1.5 bar, 2 bar and 3 bar, respectively. After deuterium absorption, the samples were furnace cooled to room temperature at roughly 5 °C/min. The amount of deuterium absorption was measured based on the ideal gas equation $\Delta PV = \Delta nRT$, in which ΔP is the variation of deuterium pressure, Δn is the mole number of deuterium absorption, R is the gas constant ($8.314\ \mathrm{Jmol^{-1}K^{-1}}$) and T is the Kelvin temperature. Pressure and temperature in the chamber were monitored within the accuracy of ±0.01 bar and ±1 °C respectively.

2.3. Microstructure observation and phase analysis

For microstructure observation and phase analysis, two types of samples were sectioned after deuterium absorption. The one was the surface sample, the other was the cross section sample. These two were used to investigate the distribution of the deuteride from the surface to the center. Deuteride distribution in the cross section and surface samples was characterized by optical image, back scattered electron (BSE) image and electron back scattered diffraction (EBSD). The samples for optical observation were etched by solution with 5%HF, 15%HNO_3, and 80%water, and the sample for EBSD analysis was prepared by electrolytic polishing using an electrolyte consisting of 5% $HClO_4$ and 95% ethanol at 30 V DC and 253 K. The morphology and phase structure of the deuterides were investigated by FEI tecnai F30 at an accelerating voltage of 300 KV. Cross section foil samples were prepared by twin-jet electropolishing using an electrolyte containing 10% $HClO_4$ and 90% ethanol at 243 K, and the surface foil samples were prepared by dimple and ion thinning. Secondary ion mass spectrometry was performed to investigate the deuterium content in the deuterated sample using an ION-TOF SIMS 5 instrument with 1 kV Cs^+ ions. The secondary ion signal was collected in an area of 400 × 400 μm with a sputtering rate of 0.08 nm/s.

The phase structures of the samples were identified by Rigaku TTRIII X-ray diffractometer (XRD) using Cu K-alpha radiation. And quantitative analysis on the XRD patterns was performed using a Reflex Quantitative Phase Analysis (QPA) module in Material Studio software (V6.0) by Rietveld method. The average δ deuteride content of samples was measured by follows [45], assuming only δ deuterides precipitation:

$$V_\delta = [\mathrm{H}]_{total}\rho_{\alpha-Zr} / \left([H]_{total}(\rho_{\alpha-Zr} - \rho_\delta) + [\mathrm{H}]_\delta \rho_\delta\right) \quad (1)$$

Table 1
Chemical composition of zircolay-4 alloy used in this study.

Element	Sn	Fe	Cr	O	H	Zr
Amount of weight (wt. %)	1.2–1.7	0.18–0.24	0.07–0.13	0.125	0.004	balance