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Hydrogen permeation characteristic of nanoscale passive films formed on different zirconium alloys

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ABSTRACT

Zircalloys, rooted in their inherent passivity, are widely used as the cladding materials for light water reactors (LWRs) due to their desirable corrosion resistance against high temperature and high pressure water. The hydrogen permeation behavior on zircaloy with passive film, however, is rarely understood so far. In this work, the gaseous hydrogen permeation characteristic mainly on the defect evolution of nanoscale passive films of nanoscale passive films formed hydrothermally on different types of zirconium alloys (Zirconium, Zircaloy-4, N18 and M5) was explored and compared. Surface analytical techniques were implemented to evaluate the hydrogen permeation characteristic. The AES depth profiles showed that the as-prepared oxides were hundreds of nanometers in thickness and inward diffusion occurred upon hydrogen exposure. Electrochemical measurements suggested that the oxides formed on different types of zircalloys were of similar phase structures of monoclinic zirconia but with different oxygen vacancy concentrations. XPS results comparison confirmed that niobium enhances the hydrogen resistance of the oxides, yet tin causes degradation of the oxides in the reductive environment. In view of these analyses, the involving mechanism was first proposed and discussed on the basis of point defect reactions.

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Introduction

In light water reactors (LWR), the surface reaction of the fuel cladding with water results in the oxidation of the cladding and the subsequent release of hydrogen. Fractional released hydrogen was picked-up and diffused into the matrix, causing the formation of hydrogen precipitates. In fusion reactor

blanket, structural materials were also confronted with the similar problem of high permeation of hydrogen isotopes in the operational condition, yielding the so-called hydrogen degradation (HD) of the matrix [1].

It is well-known that HD is one of the most important issues in safety regulation for nuclear power plants since it frequently brings a substantial loss of plasticity and sometimes in a decrease in mechanical strength [2,3]. Intensive

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investigations, pertaining to the hydrides formation and hydrogen permeation through alloys, have already been reported in literature [4–7]. Thus, reduction of hydrogen permeation is an important issue to optimize the tritium balance and minimize hydrogen embrittlement of container [7,8]. An effective coating termed tritium permeation barriers (TPB) has shown significant suppression of hydrogen isotope permeability. The most commonly utilized coatings are alumina coatings, especially the alpha alumina coatings [9,10]. However, previous study has reported that the transformation to the thermodynamically stable phase of alumina coatings occurs at a high temperature (over 1000 °C), which will result in the so-called sensitization effect of the structural materials [11,12].

In the past few decades, the waterside corrosion of zircalloys has been intensively studied and passive films could be easily formed on zircalloys. Zirconium oxide layers have been reported to be conducive to resisting the hydrogen permeation due to the existence of the O–H bonds and theoretical analysis indicated that a 5 nm layer of oxides can reduce the ingress of hydrogen dramatically [13–15]. In spite of several studies using electrochemical methods made on the hydrogen permeation performance in zirconium oxide scales [16,17], the effect of alloying elements on the hydrogen permeation behavior on zircaloy with passive film, however, is rarely understood so far.

In the present study, the experimental procedure was simplified, as possible, to avoid unnecessary influences. The gaseous hydrogen permeation characteristic of oxides formed hydrothermally on different types of zirconium alloys (Zirconium, Zircaloy-4, N18 and M5) was explored. The surface morphology, phase and chemical composition distribution along the depth were studied and compared for the four different types of zircalloys. Interestingly, we found that the performance of gaseous hydrogen permeation varies with the different alloying elements and based on these phenomena, the involving mechanism was proposed and discussed.

Experimental details

The specimens used in this study are recrystallized zircalloys provided by Nuclear Power Institute of China, including zirconium, zircaloy-4 (Zr-4), N18 and M5. The dimension and chemical composition of the samples are listed in Table 1. It should be mentioned that except for Zr, the other three zircalloys all contain precipitates. Precipitates in Zr-4 are reported to be $Zr(Fe, Cr)_2$, precipitates in N18 are reported to be

$Zr(Nb, Fe)_2$ and $Zr(Nb, Fe, Cr)_2$, while the precipitate type of M5 is β -Nb [18].

Samples were mechanically ground with SiC paper of grit sizes ranging from 500 to 5000, and then polished with diamond paste down to 0.5 μ m. The microstructure of the as-received alloys was examined by a polarized light optical microscope (OM, 6XB-PC, China). Prior to OM observations, the alloys were etched using a solution of 45 vol.% H_2O + 45 vol.% HNO_3 + 10 vol.% HF.

The oxide films were prepared in an autoclave filled with pure water at 200 °C for 24 h under a saturation pressure of \sim 1.3 MPa. As for hydrogen permeation process, parts of the as-prepared samples was sealed in quartz tubes with hydrogen pressure of 5000 Pa at room temperature and then heated at 300 °C for 4 h. To make it concise, the as-prepared oxides are henceforth denoted as NH and the samples after hydrogen permeation are denoted as YH, e.g. as for Zr, the oxide layers before and after hydrogen permeation are denoted as Zr-NH and Zr-YH, respectively.

Phase identification of the oxide layers was performed with a Raman spectrometer (Lab HR Evolution, HORIBA, France) using argon ion laser excitation at 532.2 nm at room temperature. Surface morphologies of the films were examined by field emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL, Japan) with energy dispersive spectroscopy (EDS). The main elemental distribution along the cross section was measured by Auger electron spectroscopy (AES, PHI-700, ULVAC-PHI, Japan), equipped with a coaxial electron gun, CMA energy analyzer and a differentially pumped Ar ion gun. The Photoluminescence (PL) characteristic using a 325 nm laser was employed at room temperature with the same Raman spectrometer mentioned above. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoFisherSCIENTIFIC, US) was used with a monochromatic Al X-ray source of 15 kV, 45 W. The pressure during XPS analysis was less than 1×10^{-6} Pa and all spectra were referenced to C 1s peak of adventitious hydrocarbon at 284.60 eV [19]. The XPS spectra are curve-fitted with a combination of Gaussian and Lorentzian line shapes, using a Shirley-type background substraction.

All the Electrochemical results were recorded in a three-electrode cell with a universal electrochemical interface analyzer (IM6E, ZAHNER, Germany). The samples, which are also the working electrode, were embedded in a two-component epoxy resin with the platinum foil acting as the counter electrode and the saturated calomel electrode (SCE) as the reference electrode. All experiments were performed at ambient temperature in 0.1 M Na_2SO_4 . The electrochemical impedance spectroscopy (EIS) test was carried out using an excitation voltage of 10 mV (peak-to-peak) and an applied

Table 1 – Dimension and chemical composition of the as-received zircalloys

Specimens	Dimension (mm)	Alloy elements (wt.%)					Zr
		Sn	Nb	Fe	Cr	O	
#1 (Zr)	10 × 10 × 2	–	–	–	–	–	Bal.
#2 (Zr-4)	∅ 8.2 × 1.6	1.52	–	0.18	0.09	0.10	Bal.
#3 (N18)	10 × 10 × 1	1.04	0.34	0.30	0.10	0.12	Bal.
#4 (M5)	15 × 15 × 0.6	–	0.98	0.03	–	0.13	Bal.

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