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A study on the effects of dissolved hydrogen on zirconium alloys corrosion

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ABSTRACT

The effects of dissolved hydrogen on oxide phase transformation and micro-structural changes during zirconium oxide growth were investigated using Raman spectroscopy and Transmission Electron Microscopy (TEM).

Raman spectra measurements show that tetragonal zirconia develops during oxide growth and a fraction of the phase in pre-hydrided alloy is consistently lower than that of an un-hydrided one. This was observed identically in both Zircaloy-4 and Zr–1.5Nb alloys.

TEM analysis at the metal-oxide interface support that the Raman spectra changes resulted from micro-structural changes.

These results suggest that the dissolved hydrogen may cause meta-stabilization of the tetragonal phase oxide grown at the metal-oxide interface, probably by relaxing the compressive stress built up at the interface, or by modifying the stress distribution over the interface. The relaxation or modification possibly comes from the mitigation of the lattice incoherency between the metal and the oxide at the interface that is the origin of the compressive stress build-up.

1. Introduction

Since zirconium alloys were chosen as a nuclear fuel cladding material half a century ago, numerous researchers have investigated their corrosion behaviors and provided theories regarding the kinetics and mechanisms of the reaction. Despite significant progress, however, the fundamental mechanisms of corrosion kinetics remain ambiguous.

In the 1990s when extended fuel cycle operation was introduced in the nuclear industry worldwide, observation of accelerated corrosion in high burn-up fuels reinvigorated the investigations of the fundamental mechanisms again.

Several hypotheses and theories were proposed and suggested in order to explain the enhanced corrosion, including the effects of metallurgical variables [1,2], lithium hydroxide exposure [3,4], neutron irradiation [5–7], and high hydride precipitation [8–13]. Inter-related effects of redistributed hydrides with thermal feedback across the metal-oxide interface was also claimed to be one of dominating factors in the oxidation acceleration [14].

Recently, the metal-oxide interface was regarded as rate-controlling site governing the rapid oxidation transition in high burn-up fuel [15–18]. Particularly since dense hydride precipitation at the interface and a consequent corrosion rate enhancement were reported [9,10] many studies have been carried out to evaluate the behavior of hydrogen and its effects on the corrosion rate [11–13,18,20,21]. Recent PIE (Post Irradiation Examination) results confirmed that a concentrated hydride layer forms beneath the interface of zirconium alloys irradiated in PWRs (Pressurized Water Reactors) and excessive oxidation takes place in the hydrided regions of the claddings [18,19].

Currently, there are two working hypotheses to explain the precipitated hydride effects on the accelerated corrosion. One is the assumption of mechanical degradation of the oxide integrity due to hydride precipitation, and the other is the supposition of a certain modification of oxide transport properties grown in the hydrided zirconium metal [9,11–13,18].

In the mean time, it was recently revealed that protective tetragonal oxide layer initially develops at the interface due to accumulated high stress during oxide growth, and it turns into non-protective monoclinic oxide with increasing oxide thickness, thus decreasing the stress. This transformation, resulting in the loss of the protective property of the oxide is claimed to be the cause of the rapid transition of the oxidation process [17,22–25]. The tetragonal phase is known to be stable only under high stress. The minimum stress that keeps the phase stable is about 3 GPa [26]. Recently the assertion that the stress built up initially at the metal-oxide interface exceeds the threshold stress was experimentally proved [27].

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These results imply that if zirconium oxidation kinetics crucially depends on the stress-sensitive oxide phase transformation and hydride precipitates enhance the corrosion rate, precipitated hydrides or dissolved hydrogen may play a certain role in relaxing the stress thus triggering the phase transformation early at the metal-oxide interface, leading to the enhancement of the corrosion rate. A literature survey shows several cases of accelerated phase transformations of solids induced by solutes or precipitates [28–31]. These findings led us to examine the effects of dissolved hydrogen on the promotion of phase transformation.

In this study, pure zirconium, Zircaloy-4, and Zr–1.5Nb were charged with hydrogen and oxidized at relatively high temperature in an oxygen environment to solely examine the effects of dissolved hydrogen. Then, the effects of dissolved hydrogen on the phase transformation during oxide growth in the two alloys were investigated with Raman spectroscopy, and phase identifying analyses were conducted at the metal-oxide interface using TEM.

2. Experimental

2.1. Hydrogen charging and oxidation of specimens

Pure zirconium, Zircaloy-4, and Zr–1.5Nb alloy specimens were prepared for either Raman or TEM analysis. The reason that the two alloys were chosen is to examine good and poor corrosion resistant alloys for comparison. Pure zirconium was also selected in the experiment to provide a basis for comparison. All samples were ground, and polished using 600–2000 grit SiC paper and 0.3 μm α-alumina powder, and then etched for a couple of minutes in a solution of hydrofluoric and nitric acids ($H_2O:HNO_3:HF = 50:47:3$ by volume) to remove any existing oxide film.

Prior to hydrogen charging and oxidation, the specimens were rinsed in flowing water for three minutes, cleaned in acetone, and dried in an argon environment. Then a batch of specimens was pre-hydrided using a typical gaseous charging apparatus, a Sieverts' law device, operating with two independent variables, temperature and pressure. The hydrogen concentration dissolved in the specimen was analyzed with hydrogen determinater (model RH-404) from LECO Corp.

Finally both intact and pre-hydrided specimens were air-oxidized in a muffle furnace at various temperatures to grow oxide films, whose thicknesses were determined according to required conditions of the following analyses.

2.2. Procedure for Raman spectroscopy analysis

For this analysis, plate-type Zircaloy-4 and Zr–1.5Nb alloy specimens (15 mm × 15 mm × 1 mm) were prepared. Both intact and pre-hydrided specimens were air-oxidized in a muffle furnace at 600 °C in order to solely examine the effects of dissolved hydrogen. Weight gains due to the oxidation were determined to range from zero to 40 mg/dm^2.

Raman measurements were made in backscattering geometry with a LabRAM HR system (Horiba Jobin-Yvon Ltd.) fitted with a liquid nitrogen cooled CCD detector system. Raman spectra were collected under ambient conditions using a 514.5 nm wavelength line of an argon-ion laser. The spectral resolution of the system was 0.3–1.0 cm^{-1} and the focal depth of the detector was 800 mm.

A specimen was placed directly on the stage of an optical microscope and an objective lens was controlled for the laser beam to focus on a particular point. The spectral range employed in this study was from 100 to 600 cm^{-1}.

2.3. Procedure for TEM analysis

TEM examinations of the metal-oxide interface were performed on the oxidized pure zirconium and Zircaloy-4 specimens, with and without pre-charged hydrogen, using a Field Emission TEM (Model JEM-2100F, JEOL Ltd.) and 1 MeV High Voltage TEM (Model JEM-ARM1300S, JEOL Ltd.) in KBSI (Korea Basic Science Institute).

For the pure zirconium examination, oxides on the intact and pre-hydrided specimens were grown to 2.15 μm and 0.92 μm, respectively, and the pre-charged hydrogen concentration was 607 ppm. These specimens were cut, ground, polished, and dimpled to about 20 μm thickness. Finally the 20 nm thick TEM specimens were prepared by using a precision ion milling/polishing system. Diffraction patterns and lattice images were analyzed by a digital micrograph program attached to the instrument.

Oxide thicknesses of Zircaloy-4 specimens, both with and without pre-charged hydrogen, were about 2 μms and the pre-charged hydrogen concentration was 651 ppm. Metal-oxide interface area was examined mainly with 1 MeV High Voltage TEM. In this analysis TEM specimens were prepared with a dual beam FIB (model NOVA200, FEI Co.) in National Nono-Fab Center in Korea. The FIB procedure is illustrated in Fig. 1.

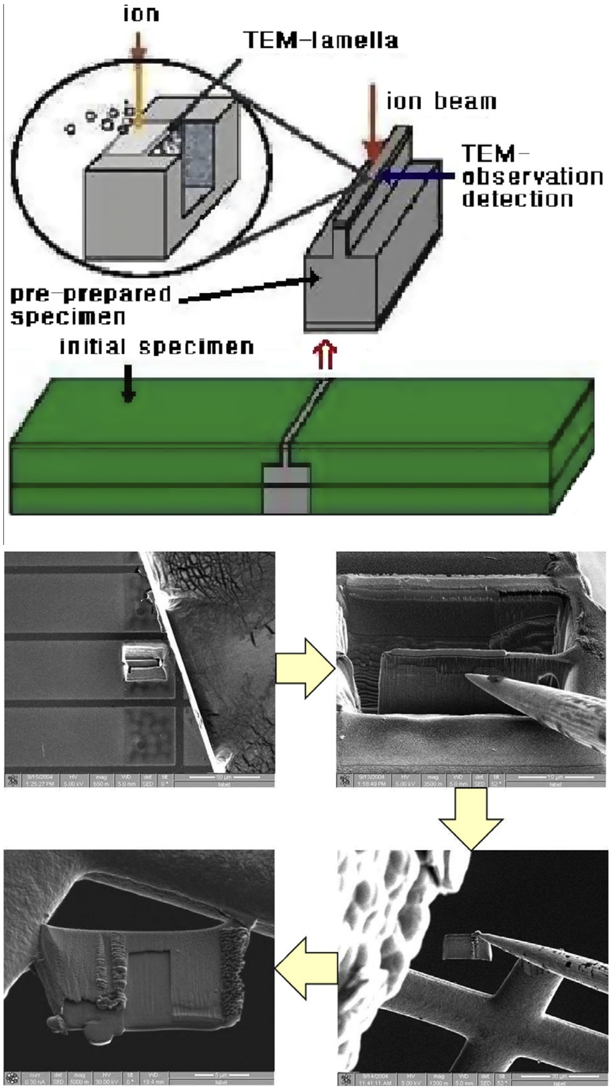

Fig. 1. FIB (Focused Ion Beam) procedure for TEM specimen preparation.