

Photoelectrochemical study of hydrogen in oxide films of Zr based alloys for fuel cladding materials of light water reactors

Masayoshi Uno*, Kazuo Takahashi, Toru Nakayama, Shinsuke Yamanaka

Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Japan

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Abstract

PEC properties of oxide film of Zr–Nb alloy with or without hydrogen were studied, and the distribution of the impurity level induced by hydrogen charging was discussed. The band gap energy of all the samples was consistent with that of ZrO₂ film. Additional PEC response was observed at lower energy than the band gap energy. This sub-band gap energy for the oxide film of hydrided samples was narrower than that for the oxide film of the alloys. It was inferred that hydrogen included into the oxide film produced the new impurity level in addition to Nb or oxygen vacancy.

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1. Introduction

Zirconium alloys have been widely used as the cladding materials of light water reactors (LWRs). In recent years, hydrogen behavior in the high burn up of nuclear fuel cladding required from the economic point of view is watched with keen notice because the oxidation of the alloy involving hydrogen absorption through the oxide film determined the lifetime of the fuel cladding. However, the chemical states of hydrogen in zirconium oxide films were not clarified.

Photoelectrochemical (PEC) measurement is now recognized as being a useful tool for investigating the electronic structure of metal oxides. Photoelectrochemical studies on the oxide films of Zr alloys have been performed and the effects of the hydrogen on the PEC properties of the oxide films have been investigated [1,2].

Recently the Zr–Nb alloys or Nb added Zry-4 are mainstreaming products in light water reactors because they have not only high corrosion resistance but also low hydrogen absorption in contrast with Zry-2 and Zry-4 [3].

In the present study, the PEC properties of oxide film of the Zr–Nb alloys with or without hydrogen were studied, and the

distribution of the impurity level induced by hydrogen charging was discussed.

2. Experimental

Specimens of 1%NbZr, 2.5%NbZr and Nb-added Zircaloy-4 were provided by Sumitomo Metal Technology Inc. The preparation process of these samples is one as described in the commercially supplied stress relieved Zry-4, and the chemical composition of these samples is summarized in Table 1. Two types of samples were prepared, oxide films on the alloys and hydrided samples. The oxide film of the alloy samples was prepared in the following way. The samples were cut to dimensions of 20 mm × 20 mm × 1 mm, polished with #1200 SiC paper and then cleaned ultrasonically in acetone. After words, the specimens were oxidized in air at 673 K for 9 h to form thin oxide film on the surface. The oxide film of the hydrided samples was prepared in the following manner. The alloy sample was polished and degreased in acetone. Then it was hydrogenated in a Sieverts' apparatus. The sample was annealed at 1073 K in vacuum (below 10⁻⁸ Torr) for 24 h. The highly pure hydrogen gas (7N) was introduced to the reaction chamber and then cooled to 673 K at 40 K/h. The cooled sample was measured by the hydrogen analyzer (Horiba EMGA) to be homogenous Zr-hydride with H/Zr ≅ 1.5. The hydrided sample was polished with #1200 SiC paper and cleaned ultrasonically in acetone. Then, it was oxidized under the same condition as that used to make oxide film of the alloy samples. The SEM observation showed that the oxide film is dense and the thickness was around 0.8 μm. There are some reports on the measurement of hydrogen concentration in oxide films on Zr alloys by 15N profiling technique [4,5]. It was reported that the implanted hydrogen retained in the oxide films after annealing 600–700 K and H/Zr was estimated to be at least 0.01. In the present study some hydrogen of hydrided samples was released during the oxidation but about 10,000 ppm (H/Zr ≅ 0.01) hydrogen might retain in the oxide films. The preparation

* Corresponding author. Tel.: +81 6 6879 7906; fax: +81 6 6879 7906.
E-mail address: uno@see.eng.osaka-u.ac.jp (M. Uno).

Table 1
Chemical composition of Zr–Nb alloys and Nb-added Zircaloy-4

Sample	Chemical composition (wt.%)							
	Sn	Fe	Cr	Nb	H	C	N	O
1%NbZr	0.002	0.038	0.002	1.00	0.0025	0.006	0.0047	0.100
2.5%NbZr	0.001	0.038	0.004	2.56	0.0032	0.008	0.0031	0.181
1%NbZry-4	1.310	0.260	0.100	1.01	0.0030	0.008	0.0037	0.201

process of working electrodes and the experimental apparatus for PEC and EIS (electrochemical impedance spectroscopy) measurements have been described before [1,2]. The EIS measurements were performed in the frequency range from 1×10^6 to 1×10^{-3} Hz with the ac amplitude of 100 mV.

3. Results and discussion

3.1. Photo-electrochemical property of zirconium oxide film

The polarization curves for the oxide films on the alloys and hydrided samples are shown in Figs. 1 and 2, respectively. The light and dark in the legend mean that the current measured

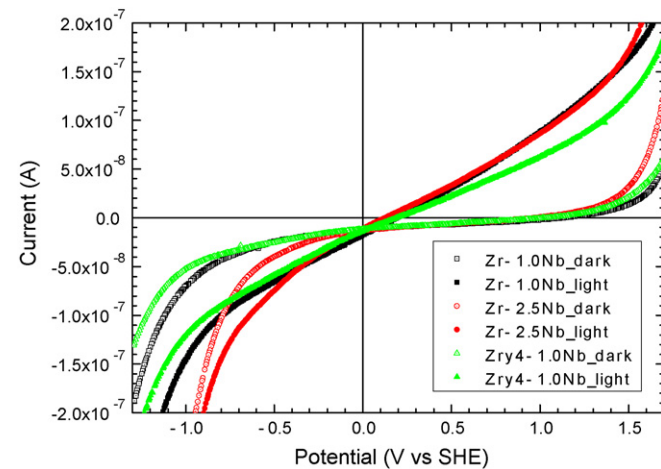


Fig. 1. Polarization curves of oxide films on Zr–Nb alloys measured with the light illumination (light) and without the light illumination (dark).

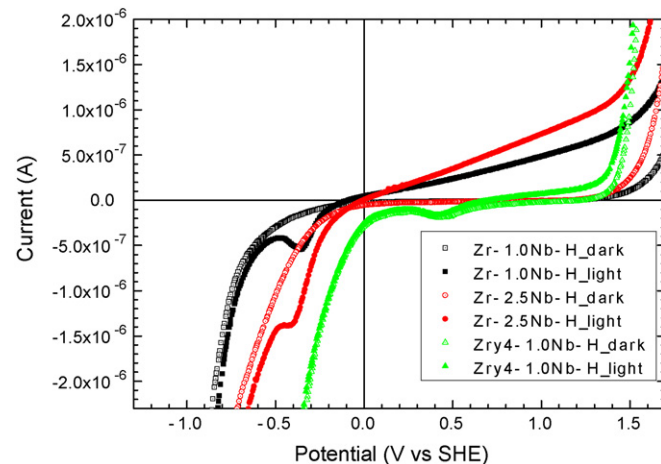


Fig. 2. Polarization curves of oxide films on hydrided Zr–Nb alloys measured with the light illumination (light) and without the light illumination (dark).

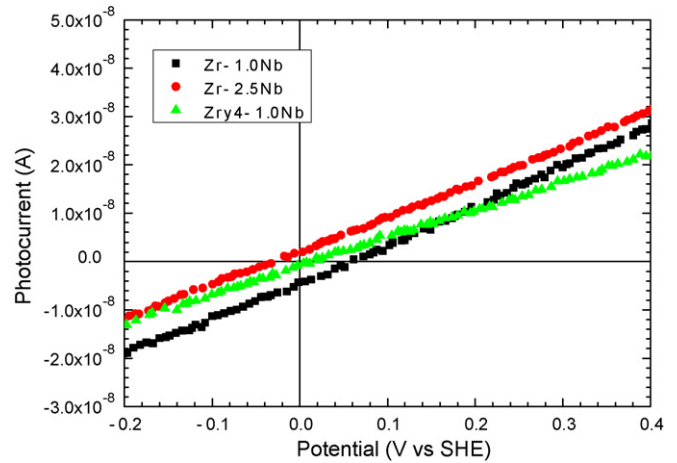


Fig. 3. Photocurrent–potential characteristics of Zr–Nb alloy oxide films.

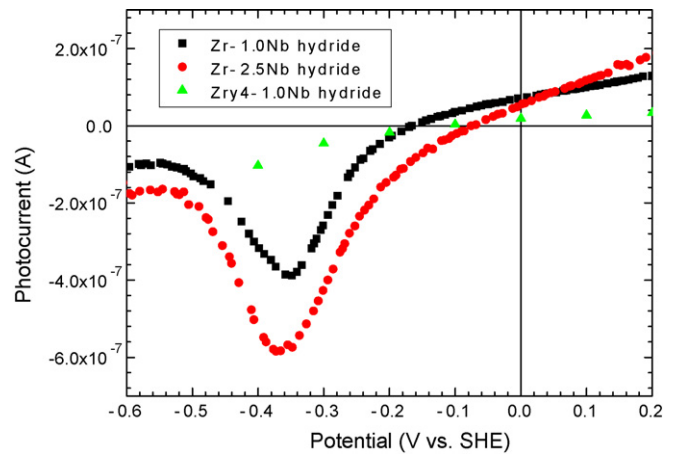


Fig. 4. Photocurrent–potential characteristics of oxide films on hydrided Zr–Nb alloys.

with light illumination and the current measured without light illumination, respectively. From the fact that the anodic current flowed by the light illumination it is found that all the oxide films showed the behavior of n-type semiconductor. The flat-band potential (U_{fb}), which is defined as the potential at which there is no band bending in the semiconductor and the anodic photocurrent vanishes, is shown in Fig. 3 for the alloys and Fig. 4 for the hydrided samples. The U_{fb} values are also shown in Table 2. The U_{fb} values for these oxide films were quite different

Table 2
Flat-band potential and band gap energy of Zr–Nb alloys and Nb-added Zircaloy-4

Sample	U_{fb} (V vs. SHE)	Sub-bandgap (eV)	Bandgap (eV)
Zr [2]	–1.1	–	4.8
Zr–1.0Nb	0.05	3.8	4.9
Zr–2.5Nb	–0.04	3.9	4.9
Zry4–1.0Nb	0.03	3.9	4.9
Hydrided Zr–1.0Nb	–0.25	3.5	4.8
Hydrided Zr–2.5Nb	–0.09	3.5	4.6
Hydrided Zry4–1.0Nb	–0.12	Undetermined	Undetermined

from that for Zr oxide film, -1.1 V versus SHE [2]. This result shows that the energy level structure is somewhat changed and the original band gap energy is reduced by Nb or hydrogen. As shown in Fig. 2, the oxide film on hydride 1%NbZr and hydrided 2.5%NbZr possessed a peak around -0.53 and -0.56 V, respectively which suggests that some chemical reactions may occur around this potential only under the illumination in contrast with oxide film on hydrided Zr or Zircalloy without Nb [1,2]. That of hydrided Zry4–1.0Nb also possessed a peak around 0.2 V. However it appears independently of the illumination. These additional peaks in the I – V diagrams suggest that the different reactions occurred in the oxide films on the hydrided Zr–Nb binary alloys and Nb added Zry-4. Further study is needed to clarify the reactions.

The band gap energy was estimated from the following equation [6–9].

$$(\Phi h\nu)^{2/n} = A(h\nu - E_g)$$

where Φ is the quantum efficiency, $h\nu$ the photon energy, A the constant value, and n is the 1/2 (for direct transition semicon-

ductor) or 2 (for indirect transition semiconductor). Quantum efficiency was expressed as:

$$\Phi = \frac{I_p h\nu}{Pe}$$

where P is the illuminating light power (W) and e is the charge of an electron, 1.6×10^{-19} (C). Fig. 5 shows plots of $(\Phi h\nu)^{1/2}$ versus $h\nu$. A linear relationship was obtained in two ranges, over and under 5 eV. This indicates that the excitation process of all the oxide films is an indirect transition. From the extrapolation of the plots over 5 eV, the band gap energy was estimated to be 4.6–4.9 eV. The sub-band gap energy was estimated in a similar way under 5 eV. These values were summarized in Table 2. This result shows that the all oxide films have an impurity levels in the original band gap because the value of 4.6–4.9 eV agrees well with previously reported band gap energy for ZrO_2 films, 4.8 eV [1,2,10,11]. It suggests that the sub-band was formed by doped elements or hydrogen or oxygen vacancy. The sub-band gap of oxide films on the hydrided samples is smaller than that of oxide films for the alloys. This may be attributed to the formation of

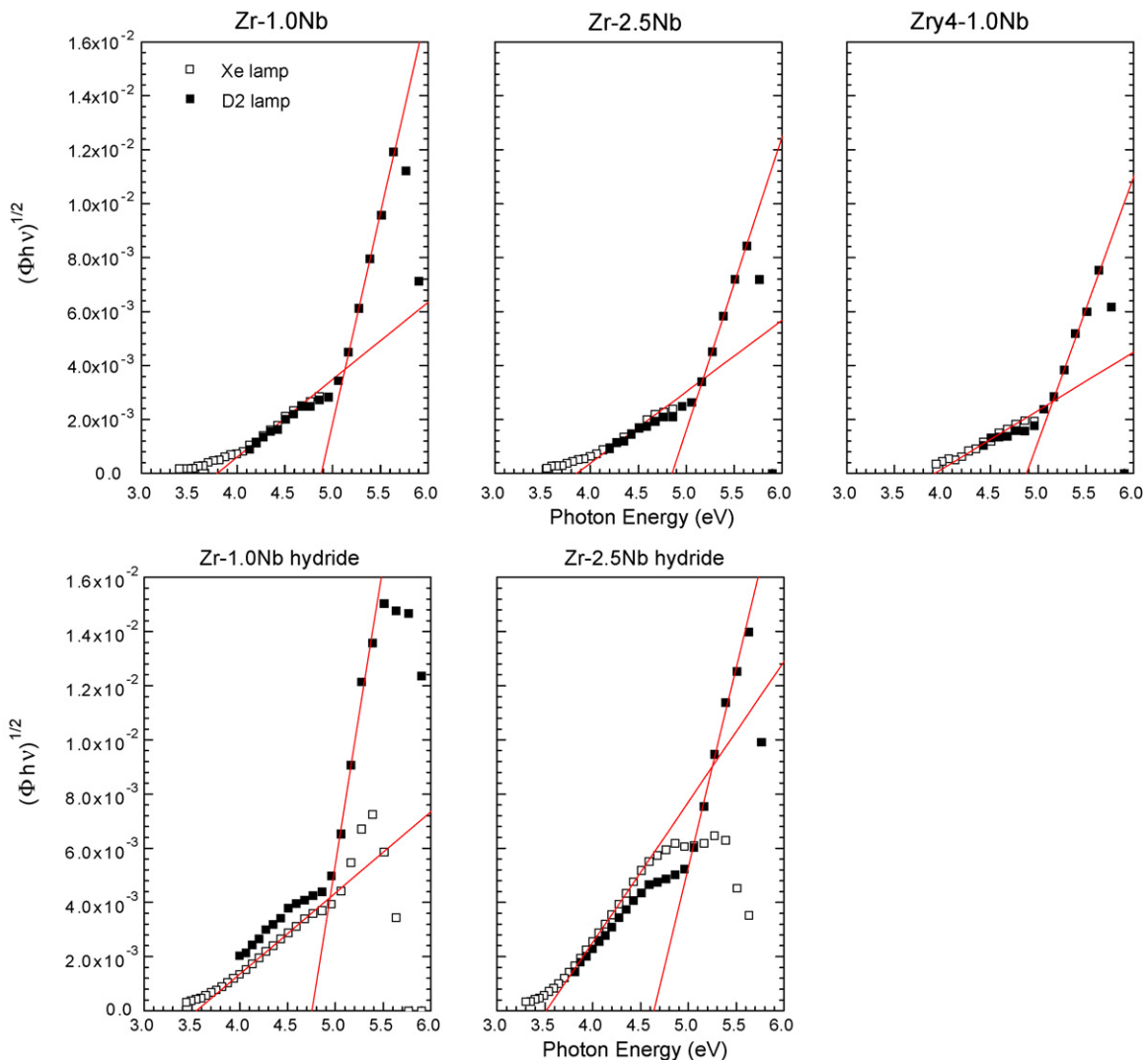


Fig. 5. Plots of $(\Phi h\nu)^{1/2}$ versus photon energy for oxide films on Zr–Nb alloys and hydrided Zr–Nb alloy.

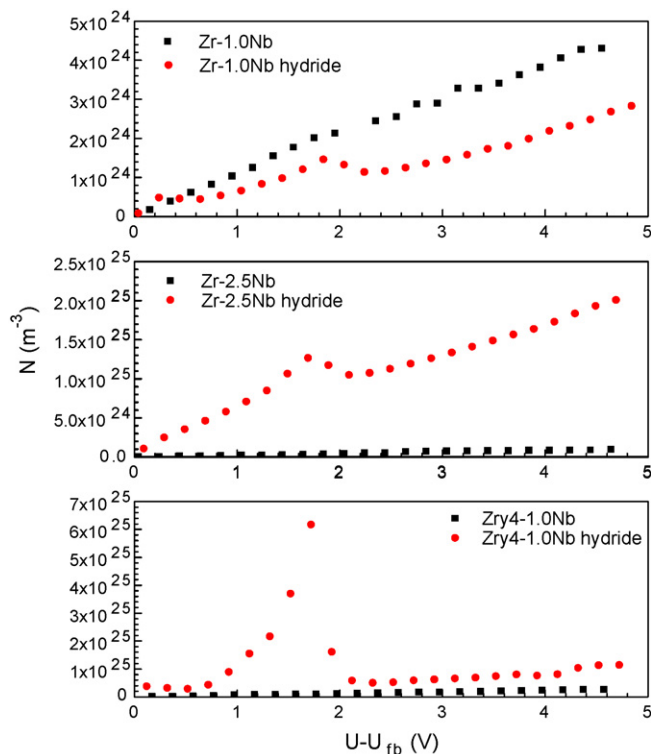


Fig. 6. Mott–Schottky plots of oxide films on Zr–Nb alloys and hydrided Zr–Nb alloy. The carrier density, N is shown as a function potential, $U - U_{fb}$.

additional impurity level in the band gap by the hydrogen in addition to Nb or oxygen vacancy.

3.2. Distribution of electron states induced by the hydrogen charging

In order to verify the results obtained by the PEC measurements, a distribution of the carrier density in the band gap was estimated from the EIS using the Mott–Schottky relationship. This relationship is represented by the following equation:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0 N_d} (U - U_{fb})$$

where ϵ is the dielectric constant, ϵ_0 the permittivity in vacuum and N_d (impurity density) is the carrier density. The detailed description of the Mott–Schottky analysis has been previously reported in the literature [12,13]. As seen from Fig. 6, a peak appears around 1.8 V for the oxide film on the hydrided samples. It is possibly due to the formation of hydrogen impurity level in the original band gap. The value of the sub-band gap energy calculated as $U - U_{fb}$ value of the peak in Fig. 6 for the oxide films on the hydrided samples, just below 2 eV does not agree with that derived from the PEC measurements, 3.5 eV as shown in Table 2. However, it should be noted that the EIS results is

qualitatively consistent with the PEC results that the decrease of the sub-band gap energy was explained as the new production of impurity level in band gap by the hydrogen in addition to Nb or oxygen vacancy.

4. Conclusion

Effects of hydrogen on the oxide films of the Zr–Nb alloys were studied by the PEC measurement and the Mott–Schottky analysis. From the PEC measurements, the band gap energies of all the samples were consistent with that of ZrO_2 film. Additional PEC responses were observed at lower energy than the band gap energy. It shows that the sub-band was formed by the addition of Nb, oxygen vacancy or hydrogen. The sub-band gap energies for the oxide films on the hydrided samples were narrower than those for the oxide films on the alloys. From these results, it is inferred that hydrogen included in the oxide film produces the new impurity level at lower energy in the original band gap. The distribution of the carrier density obtained by the Mott–Schottky analysis also showed that the new impurity level was formed in the band gap by the hydrogen in addition to Nb or oxygen vacancy.

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