

# Effects of electric field on hydrogen diffusion in zirconium alloy oxide layer

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Hydrogen embrittlement of zirconium alloy is the cause of reduced safety and short life of fuel cladding. In this work, the mechanism of hydrogen diffusion in zirconium alloy oxide has been studied, with a focus on electric field. The simulation and experimental results showed that the electric field produced by diffusion species affected on hydrogen diffusion, reducing the concentration near the surface.

## 1. Introduction

Zirconium alloy used for fuel cladding in nuclear reactors forms an oxide layer on the surface by reaction with coolant water, to produce hydrogen. When hydrogen moves through the oxide layer and is absorbed into the alloy, it causes hydrogen embrittlement, which leads to reduced safety and short life of the cladding. The mechanism of hydrogen migration in the oxide layer, however, has not been well known. In this work, we have considered hydrogen migration in the oxide layer to be diffusion, and have focused on the relationship with oxygen, which is also considered to diffuse in the oxide layer. A simulation of hydrogen diffusion which takes into account the electric field produced by diffusion species, has been created and compared with experimental results, to examine effects of electric field on hydrogen diffusion in the oxide layer.

## 2. Experiment

20mm × 20mm × 0.65mm Zircaloy-2 samples were oxidized in D<sub>2</sub>O steam for 4 to 64 hours at 400°C to form oxide layers about 0.5 to 1.2 μm thick, estimated from corrosion weight gains. The deuterium concentration distribution in the oxide layer was measured by using nuclear reaction analysis with a reaction of D(<sup>3</sup>He, p)<sup>4</sup>He. <sup>3</sup>He<sup>+</sup> ions accelerated by Van de Graaff accelerator at Kyoto University were injected perpendicularly into the sample, and the energy of protons generated by the reaction was measured by SSD in the 150° direction. Fig. 1 shows the schematic diagram of experimental equipment.

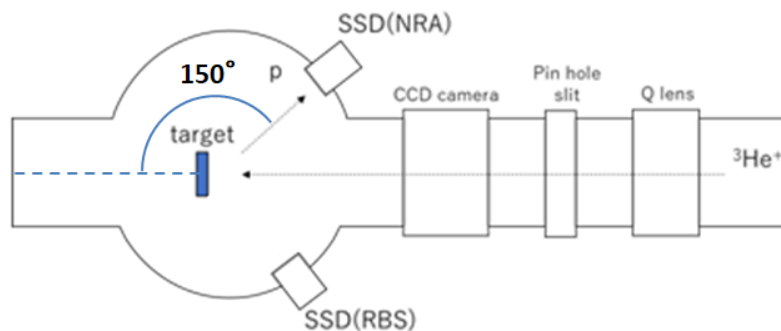


Fig.1. Schematic diagram of experimental equipment.

## 3. Simulation

The following relation (1) holds between the concentration  $C$  and the flux  $J$  of diffusion species

$$\frac{\partial C_s}{\partial t} = -\frac{\partial J_s}{\partial x} \quad (1)$$

where  $t$  is the exposure time,  $x$  is the depth from the oxide layer surface, and subscript  $s$  represents the diffusion species. When the electric field  $E$  in the oxide layer is considered, the flux  $J$  is expressed by the following equation (2)

$$J_s = -D_s \frac{\partial C_s}{\partial x} + \mu_s E C_s \quad (2)$$

where  $D$  is the diffusion coefficient and  $\mu$  is the mobility [1]. The mobility  $\mu$  depends on the diffusion coefficient  $D$ . The electric field  $E$  produced by diffusion species can be obtained from the following equation (3)

$$E(x) = E_0 + \Gamma \frac{4\pi e}{\varepsilon \varepsilon_0} \int_0^x \left( \sum_s Z_s C_s(x) \right) dx \quad (3)$$

where  $E_0$  is the electric field at the oxide-metal interface,  $\Gamma$  is the coefficient which represents the degree of contribution from electric charge of diffusion species,  $e$  is the elementary charge,  $\varepsilon$  is the relative permittivity,  $\varepsilon_0$  is the permittivity of vacuum, and  $Z$  is the valence of diffusion species [2]. Substituting Eq. (2) into Eq. (1), the diffusion equation considering electric field is derived. This equation was analytically solved using the implicit method, one of the finite difference methods, to obtain the concentration distributions of hydrogen and oxygen.

#### 4. Results and discussions

In Fig. 2, the simulations are compared with the experimental results. Here, the cases of 4 hours-oxidation are shown as representative. In the simulation considering electric field in the oxide layer, shown in Fig. 2 (a), the calculation and experimental results corresponded relatively well. On the other hand, the simulation without considering electric field, shown in Fig. 2 (b), did not replicate the experimental results, as the surface concentration of deuterium was obviously larger. It suggests that the diffusion of hydrogen in the oxide layer is affected by the electric field produced by the diffusion species. It is considered that hydrogen near the surface diffuses toward the metal more quickly due to electric field as driving force, to reduce the surface concentration.

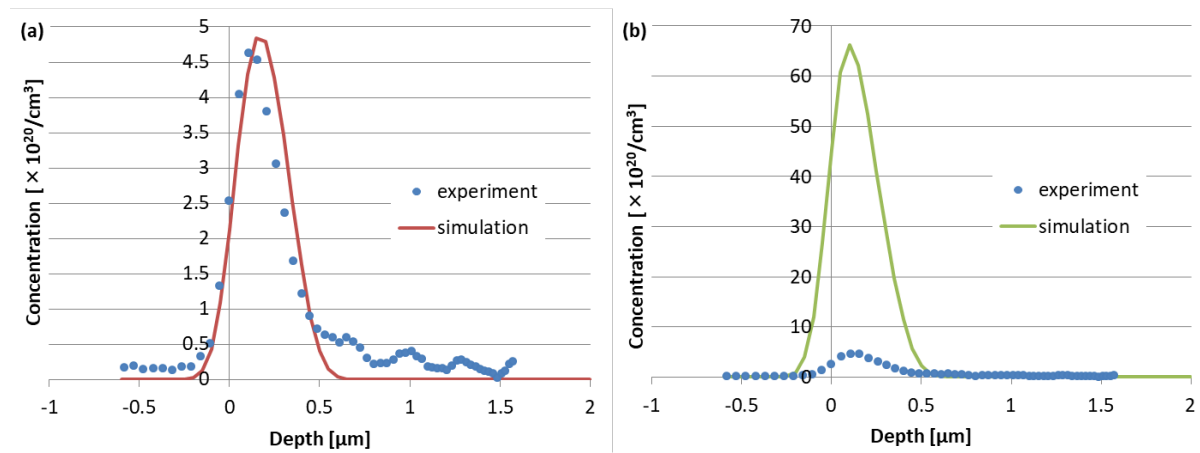


Fig.2. Deuterium concentration distribution in the oxide layer.

A line represents the simulation (a) considering electric field; (b) without considering electric field.

#### References

- [1] A. T. Fromhold, Jr., Journal of Physics and Chemistry of Solids, Vol. 33 (1972) 95-120.
- [2] A. Couet, A. T. Motta, A. Ambard, Corrosion Science 100 (2015) 73-84.