



# Observation of the spatial distribution of hydrogen in Zircaloy-2 oxidized in H<sub>2</sub>O steam at 723 K by a technique of tritium microautoradiography

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## Abstract

The spatial distribution of hydrogen in Zircaloy-2, which was oxidized in H<sub>2</sub>O steam at 723 K and quenched down to room temperature, was examined by a technique of tritium autoradiography. Tritium was introduced into the specimen through the oxide layer by the cathodic charging method using tritium water at room temperature. The radiograph of the cross-section was observed by a scanning electron microscope. Hydrogen was densely distributed on the grain boundary and in the grain of the inner base alloy, but it was scarcely distributed in the oxide layer. Hydrogen was locally distributed, however, in the region corresponding to the intermetallic precipitates embedded in the oxide layer. The mechanism of penetration of tritium through the oxide layer during the cathodic charging was discussed. © 1997 Elsevier Science B.V.

## 1. Introduction

The hydrogen pickup of zircaloy during the oxidation in aqueous media is an important phenomenon from the viewpoint of degradation of the mechanical properties of fuel claddings of nuclear reactors. Up to the present, numerous studies have been reported on the basis of many kinds of experimental technique<sup>1</sup>. Among them, however, studies with respect to the spatial distribution of hydrogen picked up in the zircaloy have been scarce despite that such information is important to clarify the mechanism of degradation of the mechanical properties due to hydrogen embrittlement and to clarify the atomistic mechanism of hydrogen pickup during reactor service. This may be ascribed to a situation that the experimental method to examine the hydrogen spatial distribution with a high resolution has not been easily available. Tritium autoradiography is such an experimental method, which gives us information of the spatial distribution of hydrogen with

high spatial resolution provided that an observation is carried out by an electron microscope. This method has previously been used to examine the tritium distribution in zircaloy oxidized in tritium water by Roy [2] and Cox and Roy [3]. In their studies, however, sufficient high resolution was not achieved, because they used an optical microscope.

In the present study, we have examined the spatial distribution of hydrogen in zircaloy on the basis of the tritium autoradiography with a high resolution by making use of a scanning electron microscopy, in which we have tried an experimental technique of cathodic charging method to introduce tritium into a zircaloy specimen which is beforehand oxidized in steam at high temperatures. Roy [2] and Cox and Roy [3] performed the tritium autoradiography for the specimens, in which tritium was introduced during the oxidation in tritium water at high temperatures. In the present experiment, tritium is introduced into the specimens through the oxide layer at room temperature after the specimens are oxidized in H<sub>2</sub>O steam at 723 K. The validity of this technique is based on the assumption that the introduced tritium may occupy the same sites as those of hydrogen which penetrates into the specimen during the oxidation, and that the cathodic charging procedure does not alter the hydrogen distribution. An advan-

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<sup>1</sup> Many bibliographies are referred in the review article in Ref. [1].

tage of the present technique is that oxidation using tritium water is not necessary.

## 2. Experimental

The rod of Zircaloy-2, whose chemical composition is summarized in Table 1, was annealed in a vacuum in the  $\beta$  phase region (1373 K) for 0.5 h and cooled at very small rate to increase the size of the precipitates. The detailed procedure of the heat treatment has been described in a previous paper [4]. Then, the disk-type specimens (2 mm in thickness, 8.5 mm in diameter) were cut from the rod. The specimens were mechanically polished with abrasive papers and finished by polishing with 0.3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder. The microstructure of the specimens was examined by a secondary electron microscope (SEM) as shown in Fig. 1. The intermetallic precipitates are mostly observed on grain boundaries. According to our previous study [4] based on the Auger electron spectroscopy, the chemical composition of these large intermetallic precipitates is of a type of  $\text{Zr}_2(\text{Fe},\text{Ni})$ : The size of intermetallic precipitates of a type of  $\text{Zr}(\text{Fe},\text{Cr})_2$  is not increased significantly by the present heat treatment.

The specimens were oxidized in 0.1 MPa  $\text{H}_2\text{O}$  steam at 723 K for 50 h. The oxygen weight gain was 4.0  $\text{g}/\text{m}^2$  which corresponded to the thickness of oxide film of 2.7  $\mu\text{m}$ . The amount of hydrogen picked up in the specimen prepared in this manner was measured by the vacuum extraction method as 0.067  $\text{g}/\text{m}^2$  which corresponded to 16 mass ppm of the hydrogen concentration in the base alloy. The detailed procedure of the measurement has been described in a previous paper [5].

Tritium was introduced into the specimens through the oxide film by the cathodic charging method at room temperature. A small part of the oxide film was removed by mechanical polishing, and a stainless steel lead wire was connected directly to the base alloy. The specimens were immersed in 0.5 N NaOH solution containing 3.6  $\text{TBq}/\text{m}^3$  of tritium, and the base alloy was polarized in the cathodic direction. The current density was adjusted as 100  $\text{A}/\text{m}^2$ , and the duration time of charging was 1 h. The radioactivity of tritium and the amount of hydrogen introduced in this manner were 130 Bq and 0.024  $\text{g}/\text{m}^2$ , respectively. The procedure to measure the radioactivity of tritium was described in the previous paper [5]. The total amount of hydrogen picked up during the oxidation and the cathodic charging was 0.091  $\text{g}/\text{m}^2$  which corre-

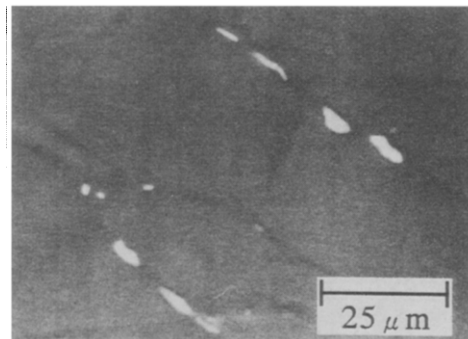


Fig. 1. Microstructure of Zircaloy-2 specimen.

sponded to 22 mass ppm of hydrogen concentration in the base alloy.

The specimens were cut in an axial direction by a micro-saw, and the cross-section was mechanically polished in the manner described above and etched by a solution of nitric and hydrofluoric acid. The thin collodion film, whose thickness was 17 nm, was placed on the cross-section by dipping the specimen in collodion diluted by ethanol. The role of this collodion film is to avoid direct contact of the specimens with the AgBr grains in the radiographic emulsion.

The monolayer of the radiographic emulsion (Konica NR-M2), in which the diameter of the AgBr grains was 0.14  $\mu\text{m}$ , was placed on the collodion film by a wire-loop method: A loop made of stainless steel wire was dipped in the emulsion diluted by deionized water, and the thin film of the emulsion was held in the loop. The thin film of emulsion was placed on the cross-section of the specimens by passing the specimens through the loop.

The specimens were kept in a light-tight box at room temperature for 7 days to expose the emulsion to the  $\beta$ -ray from tritium. Then, the specimens were dipped in a developer solution and then in a fixer solution. The AgBr grains exposed by the  $\beta$ -ray were turned by the development into Ag grains whose diameter was 0.3  $\mu\text{m}$ . The distribution of Ag grains was observed by the SEM.

## 3. Results and discussion

A SEM photograph of the obtained radiograph is shown in Fig. 2, in which white spots correspond to Ag grains. The characteristics of this radiograph are summarized as follows: Ag grains are observed in the inner region of the base alloy but sparsely observed both in the oxide layer and the thin base alloy layer beneath the oxide layer. An enlarged photograph of the radiograph of the region corresponding to the intermetallic precipitates embedded in the oxide layer is shown in Fig. 3, in which Ag grains are locally observed like bunches of grapes. These character-

Table 1  
Alloy composition of Zircaloy-2 rod

Element	Sn	Fe	Cr	Ni	O	Zr
Content (mass%)	1.31	0.18	0.09	0.06	0.13	bal.

istics suggest that hydrogen is densely distributed on the grain boundary and moderately in the grains of the inner base alloy. Hydrogen is also locally distributed in the region corresponding to the precipitates embedded in the oxide layer. It should be noted here that hydrogen is not necessarily absent in the region where Ag grains are not observed. Under the conditions of tritium activity used in the present experiment and present exposure time, hydrogen concentration more than 0.1 atomic ratio of H/Zr is at least necessary for making one Ag grains observable in a region of  $3 \times 3 \mu\text{m}^2$  when we assume that one  $\beta$ -ray reduces one Ag atom without fail.

Next, we shall discuss the chemical state of hydrogen which is observed in the present radiograph. In the case of hydrogen present on the grain boundary, two kinds of states can be supposed: one is solid solution or hydride of the intermetallic precipitates because intermetallic precipitates are mostly present on the grain boundary as is seen in Fig. 1 and the strong chemical affinity of these intermetallic compounds to hydrogen is well known. It has been reported that  $\text{Zr}(\text{Fe},\text{Cr})_2$  absorbs hydrogen up to  $\text{Zr}(\text{Fe},\text{Cr})_2\text{H}_3$  without changing its crystal structure [6,7], and that  $\text{Zr}_2\text{Ni}$ , which is a prototype of  $\text{Zr}_2(\text{Fe},\text{Ni})$ , absorbs hydrogen to form  $\text{ZrNiH}_{2.5}$  and  $\text{ZrH}_2$  [8]. The other possible state is the hydride of the matrix zirconium  $\text{ZrH}_2$ , because the hydrogen content in the present specimen exceeds the solubility limit at room temperature and such hydride must preferably precipitate on the grain boundary. The solubility limit of hydrogen at room temperature is calculated as 0.13 mass ppm from the solubility equation  $C_L = 5.17 \times 10^4 \exp(-3779/T)$  reported by Slattery [9], which is sufficiently smaller than the present hydrogen content. Summarizing these data, the present radiograph can be interpreted as follows: the relatively large white spots on the grain boundary may represent the hydrogen at the sites in the intermetallic precipitates and small ones may represent the hydrogen forming  $\text{ZrH}_2$ .

On the other hand, the chemical state of hydrogen observed in the grains of base alloy may be predominantly

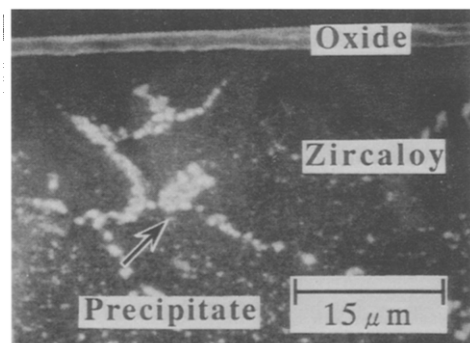


Fig. 2. Tritium microautoradiograph of cross-section of Zircaloy-2 specimen oxidized in steam and tritiated by cathodic charging method.

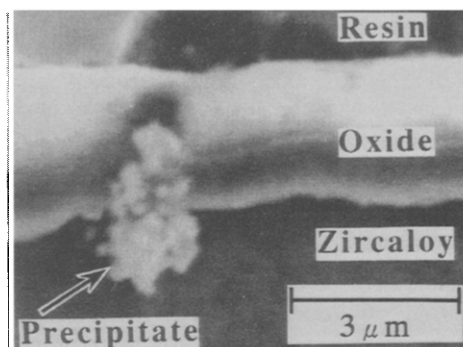


Fig. 3. Tritium microautoradiograph of intermetallic precipitate embedded in oxide layer.

of a form of  $\text{ZrH}_2$ , because the intermetallic precipitates are mostly present on the grain boundary and scarcely observed in the grains as is seen in Fig. 1.

The result that white spots are scarcely observed in the thin base alloy region beneath the oxide layer may be explained as follows: the oxygen concentration in this region may reach solubility limit, which is known to be about 29 at.% below 1073 K [10]. The existence of these oxygen atoms may reduce the solubility of hydrogen and may suppress the precipitate of hydride  $\text{ZrH}_2$ . Such depletion of hydrogen in this thin alloy layer was also reported by Roy [2].

We shall discuss the mechanism of penetration of tritium into the inner region of alloy through the oxide layer during the cathodic tritium charging at room temperature. In the present case, there may be no possibility that intermetallic precipitates supply both the direct electronic and hydrogen transport paths which bridge the oxide layer from its surface to the base alloy. In order to confirm this, the cathodic tritium charging experiment was also carried out for the specimen, in which the size of the intermetallic precipitates was very small before oxidation and recognizable precipitate was not present in the oxide layer after oxidation. The obtained autoradiograph of this specimen showed that tritium penetrated into the inner base alloy through the oxide layer, though the total amount of tritium penetrating into the base alloy is smaller than that of the specimen with larger size of precipitate. Therefore, it is beyond doubt that tritium is transported through the  $\text{ZrO}_2$  phase and that the intermetallic precipitates embedded in the oxide layer play a role of a supplementary expressway for the hydrogen transportation. The diffusion coefficient  $D$  of hydrogen in the  $\text{ZrO}_2$  phase at room temperature is evaluated as  $2 \times 10^{-23} \text{ m}^2/\text{s}$  from the data reported by Austin et al. [11]. The diffusion coefficient of hydrogen in the present intermetallic precipitates must be larger than such value, though literature values are not available. It should be noted here that the above mentioned diffusion coefficient of hydrogen in the  $\text{ZrO}_2$  phase seems to be too

small to explain the penetration depth observed in the present experiment. The average penetration depth of tritium  $(2Dt)^{1/2}$  during time  $t$  is calculated as  $4 \times 10^{-10}$  m for the cathodic charging process (1 h). This value is too small to explain the present penetration depth: The thickness of the present oxide layer is  $2.7 \times 10^{-6}$  m. The penetration depth is at most calculated as  $5 \times 10^{-9}$  m even if we assume that the present penetration was realized during the exposure time (7 days). Thus, in either case, the calculated tritium penetration depth is smaller than the observed one. We can suppose two possibilities for the origin of this discrepancy: One is that the diffusion coefficient reported by Austin et al. [11] cannot be applied to the present case. This may be likely if the microstructure of the present specimen is quite different from that of Austin et al. [11]. The other is that the certain unusual diffusion mechanism is realized in the present case. It is likely that the electrostatic force is exerted on the diffusing hydrogen. Such influence of the electrostatic force upon the diffusion of hydrogen has previously been proposed by Urquhart et al. [12] to explain the nodular corrosion of zircaloy. In the present discussion, we cannot conclude which explanation is appropriate. In any case, further examination of this problem may give us an useful information about the mechanism of the hydrogen pickup during the reactor service of zircaloy.

Finally, there may remain the question whether the observed hydrogen distribution is actually the same as that of the specimen which is oxidized in tritium water or steam. In order to solve this question, we are now planning the tritium autoradiography for the zircaloy specimens oxidized in tritium water at high temperatures.

#### 4. Conclusions

The spatial distribution of hydrogen in Zircaloy-2 disc-type specimens, which were oxidized in H<sub>2</sub>O steam at 723 K and quenched down to room temperature, was examined by a technique of tritium autoradiography. Tritium was introduced into the specimen through the oxide layer by the cathodic charging method using tritium water at room temperature. The radiograph of the cross-section was observed by a scanning electron microscope. Hydrogen was densely distributed on the grain boundary and in the grain

of the inner base alloy, but it was scarcely distributed in the oxide layer. Hydrogen was locally distributed, however, in the region corresponding to the intermetallic precipitates embedded in the oxide layer. The mechanism of penetration of tritium through the oxide layer during the cathodic charging was discussed.

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