ELSEVIER

Journal of Nuclear Materials 248 (1997) 311–314

journal of nuclear materials

Influence of size distribution of $Zr(Fe,Cr)_2$ precipitates on hydrogen transport through oxide film of Zircaloy-4

Y. Hatano [a,*], R. Hitaka [a], M. Sugisaki [a], M. Hayashi [b]

[a] Department of Nuclear Engineering, Faculty of Engineering, Kyushu University, Fukuoka 812-81, Japan
[b] Technical Development Department, Nuclear Fuel Industries, Ltd., 950 Ohaza-noda Kumatori-cho, Sennan-gun 590-04, Japan

Abstract

The hydrogen uptake behavior of two types of Zircaloy-4 specimens containing fine or coarse $Zr(Fe,Cr)_2$ precipitates was studied at 623–723 K in the pre-transition period of oxidation in steam. The amount of hydrogen uptake of the specimen containing fine precipitates was smaller than that of the specimen containing coarse ones, and the former was independent of the oxidation temperature while the latter increased with decreasing temperature. These results were successfully explained with the model that the $Zr(Fe,Cr)_2$ precipitates remaining unoxidized act as the short-circuiting route in the hydrogen transport through the oxide film. The amount of hydrogen uptake of the present Zircaloy-4 specimens containing coarse precipitates was larger than that of the Zircaloy-2 specimens containing comparable sizes of precipitates. This was attributed to the fact that the concentration of precipitates remaining unoxidized in the oxide film of Zircaloy-4 was higher than that of Zircaloy-2. © 1997 Elsevier Science B.V.

1. Introduction

Reduction of the amount of hydrogen uptake of zircaloy during the operation of light water nuclear reactors is one of the important subjects to retain the favorable mechanical property of the fuel claddings, and, hence, numerous studies have been reported for the hydrogen uptake behavior of zircaloy [1]. However, up to the present, the hydrogen uptake mechanism of zircaloy has not been fully clarified. It has been at least ascertained, however, that the size distribution of the intermetallic precipitates such as $Zr_2(Fe,Ni)$ and/or $Zr(Fe,Cr)_2$ have an influence on the rate of hydrogen uptake. Generally speaking, the rate of hydrogen uptake may be controlled by two factors, i.e., the thickness and the hydrogen permeability of the dense oxide layer. Therefore, it is important to clarify the influence of the size distribution of the precipitates on these two factors.

Recently, we have studied the role of intermetallic precipitates in the hydrogen transport through the oxide film. In a previous paper [2], we have examined the influence of the size distribution of intermetallic precipitates, such as $Zr_2(Fe,Ni)$ and $Zr(Fe,Cr)_2$, on the hydrogen uptake behavior of Zircaloy-2. Two types of specimens containing fine or coarse precipitates were prepared with heat-treatment, and the hydrogen uptake behavior during the oxidation in steam was examined. The former specimen took up a small amount of hydrogen compared with the latter, and the amount of hydrogen uptake of the former did not show the oxidation temperature dependence while that of the latter increased with decreasing oxidation temperature. These results were attributed to the fact that the intermetallic precipitates remaining unoxidized in the oxide film act as the short-circuiting route in the hydrogen transport. The influence of $Zr_2(Fe,Ni)$ and $Zr(Fe,Cr)_2$, however, could not be separated.

In the present study, the hydrogen uptake behavior of the two types of Zircaloy-4 specimens containing fine or coarse $Zr(Fe,Cr)_2$ precipitates was examined in the pre-transition of oxidation to clarify the role of $Zr(Fe,Cr)_2$ precipitates in the hydrogen transport through the oxide film. The concentration distribution of hydrogen in the oxide film was measured with secondary ion mass spectroscopy (SIMS).

---

[*] Corresponding author. Tel.: +81-92 642 3775; fax: +81-92 642 3800; e-mail: yhatatne@mbox.nc.kyushu-u.ac.jp.

PII S0022-3115(97)00128-1

2. Experimental

2.1. Specimen preparation and oxidation

The alloy composition of Zircaloy-4 used in this study is shown in Table 1. Two different disk-type specimens (8.5 mm in diameter, 3 mm in thickness), in which the size distribution of the $Zr(Fe,Cr)_2$ precipitates was extremely different from each other, were prepared with heat-treatments, i.e., annealing in the β phase region (1323 K) for 1 h followed by water quenching or slow cooling. These heat-treatments are similar to those conducted to prepare the Zircaloy-2 specimens [2] except that the cooling rate in slow cooling was decreased from 270 to 10 K s^{-1}. The reason why the cooling rate was decreased is that the growth rate of the $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 was smaller than that of $Zr_2(Fe,Ni)$ precipitates in Zircaloy-2 and the comparable size distribution of precipitates was not obtained at the same cooling rate. The specimens treated in the former and latter way will be described hereafter as β quenched and β slow-cooled specimens, respectively. The specimens were mechanically polished with abrasive papers and finished by polishing with 0.3 μm Al_2O_3 powder.

The microstructure of the specimen was examined by the scanning electron microscopic observation of the specimen surface etched with a solution of 10% HF–45% HNO_3–45% H_2O. In the β quenched specimen, no intermetallic precipitate was observed: The intermetallic precipitate whose diameter exceeded the resolving power of SEM, 50 nm in the present study, did not exist in the β quenched specimen. In the β slow-cooled specimen, coarse intermetallic precipitates were observed at the grain boundaries. The average and maximum diameter of the precipitates were 0.5 and 1.7 μm, respectively.

The specimens were oxidized in 0.1 MPa steam at 623, 673 and 723 K for 1–4000 h. The oxygen weight gain ΔW_O with time t could be approximated by the cubic rate law: $\Delta W_O = kt^{1/3}$, where k is the rate constant. From the oxidation temperature dependence of the rate constant k, the activation energy of oxidation was estimated as 0.53 and 0.36 eV for the β quenched and β slow-cooled specimens, respectively.

The amount of hydrogen uptake was measured with a hot extraction method; the detailed procedure of the measurement has been described in a previous paper [3].

2.2. Measurement of hydrogen distribution in oxide film with SIMS

The specimens for the SIMS analysis were prepared with two steps oxidation in H_2O and D_2O steam. First, the specimens were oxidized at 673 K in 0.1 MPa H_2O steam up to about 1.8 g m^{-2} in the oxygen weight gain (1.2 μm in the thickness of oxide film), and then oxidized in 0.1 MPa D_2O steam up to about 2.0 g m^{-2} in the total oxygen weight gain (1.3 μm in the thickness of oxide film).

Table 1
Alloy composition of Zircaloy-4 rod

Element	Sn	Fe	Cr	O	Zr
Content (mass%)	1.56	0.21	0.10	0.13	bal.

In the analysis, 16 keV argon ion beam which was 600 μm in diameter was employed as the primary ion beam, and D^+ ion and $^{16}O^+$ ion were detected. The diameter of the ion beam was larger than the diameter of the precipitates and the distance between the precipitates, and, hence, deuterium in both the matrix zirconium oxide and the $Zr(Fe,Cr)_2$ precipitates remaining unoxidized in the matrix zirconium oxide was detected.

The D^+ ion current was converted to the deuterium concentration by measuring the radioactivity of tritium being present in the oxide film of the specimens oxidized in tritiated steam instead of D_2O steam. The method of conversion was described in detail in the previous paper [2].

3. Results

3.1. Hydrogen uptake

The hydrogen uptake behavior of β quenched and β slow-cooled specimens is shown in Fig. 1. In this figure, the amount of hydrogen uptake of the β quenched and β slow-cooled specimens of Zircaloy-2 is also plotted for comparison. The amount of hydrogen uptake of the present β quenched specimen is smaller than that of the present β slow-cooled specimen, and the former is independent of the oxidation temperature while the latter increases with decreasing temperature.

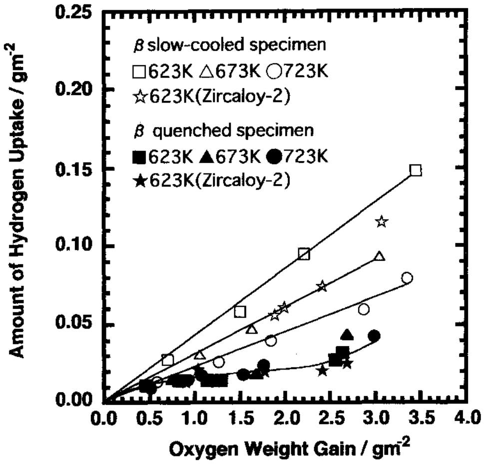

Fig. 1. Hydrogen uptake of β quenched and β slow-cooled specimens.

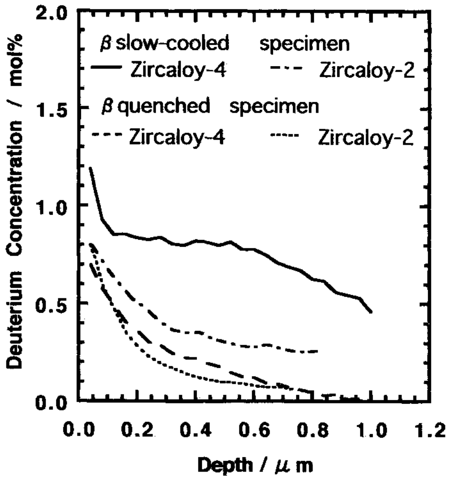

Fig. 2. Concentration profile of deuterium in the oxide film formed on β quenched and β slow-cooled specimens at 673 K.

It should be noted that the amount of hydrogen uptake of the β slow-cooled specimen is larger for Zircaloy-4 than for Zircaloy-2 while that of β quenched specimen of Zircaloy-4 and -2 are comparable to each other.

3.2. Concentration distribution of hydrogen in the oxide film

The distribution of deuterium concentration (D/ZrO_2 in mol%) in the oxide film of both types of specimens is shown in Fig. 2. In this figure, the deuterium concentration in the oxide film of the β quenched and β slow-cooled specimens of Zircaloy-2 measured in the similar procedure is also plotted for comparison. The deuterium concentration is clearly gradient in the oxide film of both types of the present specimens. This indicates that the rate controlling process of hydrogen uptake is the transport of hydrogen through the oxide film and not other processes such as dissolution at the oxide surface. The deuterium concentration of β quenched specimen is lower than that of β slow-cooled specimen.

It should be noted that the deuterium concentration in the oxide film of β slow-cooled specimen is higher for Zircaloy-4 than for Zircaloy-2 while that in the oxide film of β quenched specimen of Zircaloy-4 and -2 are comparable to each other.

4. Discussion

The hydrogen uptake behavior of Zircaloy-4 shown in Fig. 1 is similar to that of Zircaloy-2 except that the amount of hydrogen uptake of the β slow-cooled specimen is larger for Zircaloy-4 than for Zircaloy-2. This indicates that the mechanism of hydrogen transport through the oxide film of Zircaloy-4 and -2 is basically similar. The detailed model of hydrogen transport through the oxide film was given in the previous paper [2], and hence only a brief description of the model is given here.

It has been known that the $Zr(Fe,Cr)_2$ precipitates are accommodated in the oxide film in an unoxidized state and then gradually oxidize [4–7]. The hydrogen released from water molecules dissolves in the oxide film and diffuses through the zirconium oxide phase into the $Zr(Fe,Cr)_2$ precipitates remaining unoxidized since the chemical affinity of $Zr(Fe,Cr)_2$ to hydrogen is appreciably large [8,9]. The precipitates may be saturated by hydrogen immediately since the concentration of the precipitates is appreciably low. The concentration of $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 can be estimated as 0.26 mol% from the alloy composition provided that almost all Fe and Cr form precipitate. After the precipitates are saturated, the hydrogen in the precipitates again dissolves in the zirconium oxide phase at the downstream side, i.e., the base alloy side, of the precipitates and diffuses to the base alloy. Here the $Zr(Fe,Cr)_2$ precipitates may act as the fast transport route of hydrogen, i.e., the short-circuiting route in the hydrogen transport, and may thereby enhance the hydrogen uptake since the diffusivity of hydrogen in this intermetallic is considered to be appreciably large owing to the fact that $Zr(Fe,Cr)_2$ absorbs a large amount of hydrogen rapidly even at low temperature (< 373 K) [8,9]. In the case of β quenched specimen, the precipitates are fine, and hence they may be completely oxidized immediately after the oxygen potential in the oxide film becomes high enough for the oxidation of the precipitates. On the other hand, in the case of β slow-cooled specimen, the core region of coarse precipitates may remain unoxidized even at the oxygen weight gain of 3.5 g m^{-2}. This may be the reason why the amount of hydrogen uptake of the β quenched specimen was smaller than that of the β slow-cooled specimen. The difference between the deuterium concentration in the oxide film of β quenched and β slow-cooled specimens observed in Fig. 2 may correspond to the amount of deuterium being present in the precipitates remaining unoxidized in the oxide film of β slow-cooled specimen.

The present result that the amount of hydrogen uptake of the β slow-cooled specimen increased with decreasing oxidation temperature can be interpreted as follows: The relative oxidation rate of the precipitates to the matrix zirconium decreases with the temperature and, hence, the concentration of precipitates remaining unoxidized in the oxide film increases with decreasing temperature at the same oxygen weight gain. This mechanism was confirmed for Zircaloy-2 by measuring the electronic conductivity of the oxide film [2]. In the case of β quenched specimen, the temperature dependence of hydrogen uptake is determined by that of the hydrogen transport rate in the matrix zirconium oxide and the oxidation rate provided that the contribution of precipitates to the hydrogen transport is negligibly small. Hence, the present result that the amount of hydrogen uptake of β quenched specimen was independent of the oxidation temperature may indicate that the activation energy of hydrogen transport in the matrix zirconium oxide is comparable to the activation energy of the oxidation of β quenched specimen, 0.53 eV.

The reason why the amount of hydrogen uptake of the β slow-cooled specimen was larger for Zircaloy-4 than for Zircaloy-2 is considered to be that the concentration of precipitates remaining unoxidized in the oxide film is higher for the former than for the latter because of the following facts:

(1) The deuterium concentration in the oxide film of β slow-cooled specimen was higher for Zircaloy-4 than for Zircaloy-2 while that in the oxide film of β quenched specimen of Zircaloy-4 and -2 were comparable to each other. This indicates that the amount of hydrogen being present in the precipitates remaining unoxidized in the oxide film of β slow-cooled specimen is larger for Zircaloy-4 than for Zircaloy-2.

(2) The maximum amount of hydrogen that $Zr(Fe,Cr)_2$ can absorb is considered to be comparable to or smaller than that $Zr_2(Fe,Ni)$ can do. The maximum amount of hydrogen absorbed by a molecule of $Zr(Fe,Cr)_2$ is known to be three atoms [8,9], and that by a molecule of $Zr_2(Fe,Ni)$ is considered to be 3–4.5 atoms since Zr_2Fe and Zr_2Ni are known to absorb up to three and 4.5 hydrogen atoms per a molecule, respectively [10].

The concentration of $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 can be estimated as 0.26 mol% as mentioned above, and that of $Zr_2(Fe,Ni)$ and $Zr(Fe,Cr)_2$ precipitates in Zircaloy-2 can be estimated as 0.23 and 0.16 mol% [2]; the total concentration of the $Zr_2(Fe,Ni)$ and $Zr(Fe,Cr)_2$ precipitates in Zircaloy-2 is higher than the concentration of $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4. Consequently, it is appropriate to consider that the oxidation rate of $Zr(Fe,Cr)_2$ precipitates is smaller than that of $Zr_2(Fe,Ni)$ precipitates.

In the present study, it has been confirmed that the size distribution of $Zr(Fe,Cr)_2$ precipitates controls the rate of hydrogen transport through the oxide film in the pre-transition region. Then, the next problem is to clarify the influence of size distribution of the precipitates on the breakdown behavior of oxide film.

5. Conclusions

(1) The hydrogen uptake behavior of two types of Zircaloy-4 specimens containing fine or coarse $Zr(Fe,Cr)_2$ precipitates was studied in the pre-transition period of oxidation to clarify the role of $Zr(Fe,Cr)_2$ precipitates in the hydrogen transport through the oxide film.

(2) The amount of hydrogen uptake of the specimen containing fine precipitates was smaller than that of the specimen containing coarse ones, and the former was independent of the oxidation temperature while the latter increased with decreasing oxidation temperature. These results were successfully explained with the model that the $Zr(Fe,Cr)_2$ precipitates remaining unoxidized in the oxide film act as the short-circuiting route in the hydrogen transport.

(3) The amount of hydrogen uptake of the present Zircaloy-4 specimen containing coarse precipitates was larger than that of the Zircaloy-2 specimen containing comparable size of precipitates. This was attributed to that the concentration of precipitates remaining unoxidized in the oxide film was higher for Zircaloy-4 than for Zircaloy-2.

Acknowledgements

The authors would like to express their sincere thanks to Professor K. Ōgi of Faculty of Engineering, Kyushu University for use of SIMS and Mr K. Wakasugi for helpful assistance in the measurements. The present study was partly supported by a Grant-in-Aid for Scientific Research (B) of the Ministry of Education, Science, Sports and Culture, No. 02452295.

References

[1] Many bibliographies are referred in the following review article: Corrosion of Zirconium Alloys in Nuclear Power Plants, IAEA-TECDOC-684 (1993).

[2] Y. Hatano, K. Isobe, R. Hitaka, M. Sugisaki, J. Nucl. Sci. Technol. 33 (1996) 944.

[3] K. Hashizume, M. Sugisaki, K. Hatano, T. Ohmori, K. Ōgi, J. Nucl. Sci. Technol. 31 (1994) 1294.

[4] T. Kubo, M. Uno, Proc. 9th Int. Symp. on Zirconium in the Nuclear Industry, Kobe, Japan, Nov. 5–8, 1990, ASTM-STP 1132 (1991) 476.

[5] D. Pêcheur, F. Lefebvre, A.T. Motta, C. Lemaignan, J. Nucl. Mater. 189 (1992) 318.

[6] D. Pêcheur, F. Lefebvre, A.T. Motta, C. Lemaignan, D. Charquet, Proc. 10th Int. Symp. on Zirconium in the Nuclear Industry, Baltimore, MD, USA, June 21–24, 1993, ASTM-STP 1245 (1994) 687.

[7] X. Iltis, F. Lefebvre, C. Lemaignan, J. Nucl. Mater. 224 (1995) 121.

[8] D. Shaltiel, I. Jacob, D. Davidov, J. Less-Common Met. 53 (1977) 117.

[9] F. Pourarian, W.E. Wallace, J. Less-Common Met. 107 (1985) 69.

[10] R.M. Van Essen, K.H.J. Buschow, J. Less-Common Met. 64 (1979) 277.