

Modified Zircaloy-4에서 수소의 Thermotransport에 있어서 수소와 산소의 보고

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Influence of Hydrogen and Oxygen on the Thermotransport of Hydrogen in Modified Zircaloy-4

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Abstract The hydrogen redistribution induced by thermotransport at temperatures likely to be encountered in nuclear power reactors (300-340°C) was investigated in modified Zircaloy-4 alloys. Modified Zircaloy-4 alloys were prepared by altering the chemical composition of Zircaloy-4; the oxygen content of Zircaloy-4 (0.1 wt%) was increased to 0.2, 0.5 and 1.0 wt%. The heat of transport (Q^*) for hydrogen was measured by changing the initial hydrogen and oxygen concentrations. It was found that the heat of transport was not affected by increases in the initial hydrogen concentration from 63.3 to 91.7 ppm. However, the value of Q^* decreased from 6.8 to 4.5 kcal/mol as the initial oxygen concentration was increased from 0.2 to 1.0 wt%.

Keywords hydrogen redistribution, oxygen concentration, hydrogen concentration, modified Zircaloy-4, thermotransport

1. Introduction

The recent trend towards extended burn-up and high pH operation of nuclear power plants has led to an increased demand for higher corrosion resistance of nuclear fuel cladding materials as well as improvement in mechanical properties. Recently, modified Zircaloy-4 was developed by changing the chemical composition of Zircaloy-4. The tin content was decreased from 1.5 to 0.5 wt% to improve the corrosion resistance while the oxygen content was increased from 0.1 to 0.8 wt% to compensate for the decrease in strength resulting from the reduction in the tin content. The addition of oxygen caused a marked improvement in mechanical strength, and modified Zircaloy-4 containing 0.2 wt% oxygen showed better oxidation resistance than Zircaloy-4.¹⁾

Zircaloy-4 picks up hydrogen mainly from the oxidation reaction of Zircaloy-4.^{2,3)} Some of the hydrogen atoms accumulate at the ZrO_2 /matrix interface and the rest diffuse into the zirconium matrix.⁴⁾ The hydrogen dissolved in Zircaloy-4 can be redistributed in the presence of a temperature gradient.^{5,6)} During reactor operation, hydrogen

in Zircaloy-4 cladding moves towards the colder region of outer surface due to the temperature gradient between the outer and inner surface.^{5,7)} As a result, zirconium hydride is precipitated at the cold end of the cladding (the outer surface) due to the low solubility of hydrogen in Zircaloy-4. Because zirconium hydride in Zircaloy-4 can have a detrimental effect on the mechanical properties, it is important to know how the hydrogen redistributes itself during reactor operation.

In the present study, the hydrogen redistribution due to thermotransport in modified Zircaloy-4 alloys at the temperatures likely to be encountered in nuclear power reactors (300-340°C) was determined, and the heat of transport values, Q^* , were obtained for the alloys. In addition, changes in Q^* for the modified Zircaloy-4 alloys were investigated with varying the initial hydrogen and oxygen concentrations.

2. Experimental procedures

Three modified Zircaloy-4 alloys were prepared by altering the chemical composition of Zircaloy-4. The chemical compositions of these alloys are presented in Table 1. The three modified alloys contained equal

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Table 1. Chemical compositions of the specimens in the present study

Specimen	Alloying elements (wt%)						Hydrogen (ppm by wt.)
	Sn	Nb	Cr	Fe	O	Zr	H
#1 (Modified alloy-A)	0.5	0.1	0.2	0.1	0.2	Bal.	63.3 76.5 91.7
#2 (Modified alloy-B)	0.5	0.1	0.2	0.1	0.5	Bal.	64.3
#3 (Modified alloy-C)	0.5	0.1	0.2	0.1	1.0	Bal.	65.7

concentrations of Sn, Nb, Cr and Fe. The modified alloys differed only in their oxygen concentrations. The oxygen concentrations of Modified alloy-A, Modified alloy-B and Modified alloy-C were 0.2, 0.5 and 1.0 wt%, respectively. Sheet-type specimens for the thermotransport test with dimensions of 30 mm(L)×8 mm(W)×0.6 mm(t) were prepared by the procedures described in the previous study.¹⁾

Hydrogen was introduced into Zircaloy-4, Modified alloy-B and Modified alloy-C at 92.4, 64.3 and 65.7 wppm, respectively. Three different hydrogen amounts (63.3 wppm, 76.5 wppm, 91.7 wppm) were introduced into Modified alloy-A in order to investigate the effect of the initial hydrogen concentration on the thermotransport.

A platinum anode and an electrolyte of 10 vol% H₂SO₄ + 90 vol% H₂O were used for the cathodic charging of hydrogen. The current was 4 A/m² and the temperature was 80°C. After charging, the specimens were held at 340°C for 3 days in order to homogenize the hydrogen concentration in the specimens. The hydrogen-charged specimens were placed in tube furnaces with one end of each specimen at 340°C and the other at 300°C. A preliminary run with five chromel-alumel thermocouples equally spaced along the specimen indicated a constant temperature gradient. The time to reach the steady state is given approximately as the time required for all the hydrogen to be precipitated out as hydride at the cold surface,⁸⁾ namely

$$t_s = C_0 \frac{a}{J(T_c)} \quad (1)$$

where C_0 is the initial hydrogen concentration, a the length of the specimen and $J(T_c)$ the flux of hydrogen at the cold surface and is given by⁹⁾:

$$J(T_c) = \frac{DC}{RT_c^2} \{ \Delta H + Q^* \} \frac{dT}{dx} \quad (2)$$

where D is the diffusion coefficient, C the hydrogen concentration, T the temperature, R the gas constant, x the coordinate through the diffusion region, ΔH the heat of mixing of hydrogen in alpha zirconium and Q^* the heat of

transport. The time to steady state (t_s) was calculated to be around 90 days from Eq. (1), using $C_0 = 92.4$ ppm by weight, $Q^* = 7$ kcal/mol,¹⁰⁾ $D = 8.8 \times 10^{-7}$ cm²/sec,¹¹⁾ and $\Delta H = 7.6$ kcal/mol.¹²⁾

After a thermotransport of 35 days, specimens were removed and cut into slices of equal size (2 mm×8 mm×0.6 mm). These slices were analyzed for hydrogen by the hot vacuum extraction method, and the hydrogen distribution along the specimen was determined.

3. Results and Discussion

The hydrogen distribution in Modified alloy-A as a function of hydrogen concentration before the steady state is shown in Fig. 1. The terminal solid solubility (TSS) curve in Fig. 1 was retrieved from Kern's data obtained in Zircaloy-4.¹³⁾ The Kern's TSS value is in a good agreement with those obtained in zirconium by Gulbransen and Andrew¹³⁾, by Mallett and Albrecht¹⁴⁾, and by Erickson¹⁵⁾, and those in Zircaloy-2 by Sawatzky¹⁶⁾ and by Östberg.¹⁷⁾ The hydride precipitation in the two-phase region was confirmed through X-ray diffraction studies and

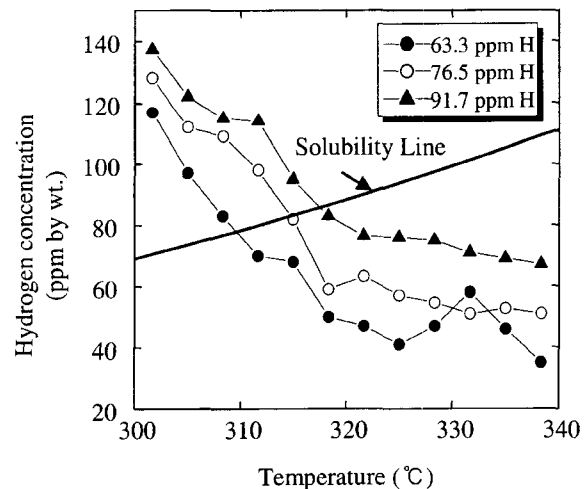


Fig. 1. Hydrogen in Modified alloy-A as a function of hydrogen concentration before the steady state.

optical micrograph observations. It can be seen in Fig. 1 that the specimen was composed of the single-phase region in which hydrogen exists in α -zirconium as a solid solution and the two-phase region in which alpha solid solution and zirconium hydride coexist. The temperature at the interface between the single-phase and the two-phase region was around 318°C. The hydrogen distribution showed an abrupt increase in the concentration at the interface between the single-phase region and the two-phase region. The hydrogen redistribution showed the two-phase region in the colder region and the single-phase region in the hotter region. The temperature at the interface between the single-phase and the two-phase region in Modified alloy-A increased from 310 to 315 and 320°C as the initial hydrogen concentration was increased from 63.3 to 76.5 and 92 ppm by weight.

The hydrogen distribution curve of Modified alloy-A was relatively smooth at the interface between the single-phase region and the two-phase region indicating a relatively small increase in concentration at the interface. Sawatzky⁸⁾ reported an abrupt increase in hydrogen concentration at the interface before steady state in Zircaloy-2. However, the increase in the hydrogen concentration measured by Sawatzky was much higher than what was seen in the present study. In Sawatzky's experiment, the temperature differential between the hot and cold ends of the specimen was larger than that used in the present experiment. When a larger temperature differential is present, a greater amount of hydrogen accumulates as hydride at the interface, which could result in an abrupt increase in the concentration at the interface. It is likely that the temperature differential used in this study was not sufficient to develop large discontinuities in the concentration profiles.

Fig. 2 shows the hydrogen distributions in the modified Zircaloy-4 alloys (Modified alloy-A, -B and -C) as a

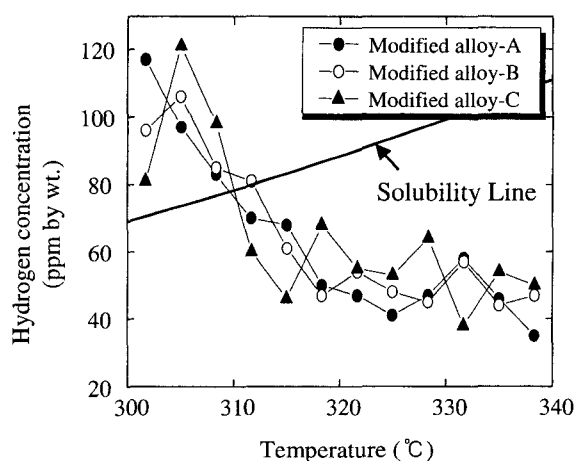


Fig. 2. Hydrogen distribution in the modified Zircaloy-4 specimens (Modified alloy-A, -B and -C) as a function of oxygen concentration before the steady state

function of the initial oxygen concentration. It can be seen from the figure that the direction of the thermotransport was from the hot to the cold end, however, the magnitude of the transport decreased as the oxygen concentration increased. Zirconium hydride precipitation at the cold end of the specimens was confirmed by XRD and OM. The temperature at the interface between the single-phase and the two-phase region in the modified Zircaloy-4 specimens was about 312°C. This temperature appeared not to be influenced by the oxygen concentration.

The basic idea of the thermotransport^{9,18)} is that an atomic flux can occur in the presence of a temperature gradient. The atomic flux is given by

$$J = -\frac{DC}{RT} \left\{ RT \frac{d \ln C}{dx} + \frac{Q^* dT}{T dx} \right\} \quad (3)$$

where D is the diffusion coefficient, C the hydrogen concentration, T the temperature, R the gas constant, x the coordinate through the diffusion region and Q^* the heat of transport. A steady state is reached when the flux caused by the concentration gradient equals that caused by the temperature gradient. Under this condition the net flow vanishes ($J = 0$) and Eq. (3) can be written as

$$\frac{d \ln C}{d(1/T)} = \frac{Q^*}{R} \quad (4)$$

It can be seen that the value of the heat of transport (Q^*) can be obtained from Eq. (4). The heat of transport is a experimentally determined parameter which describes the sign and magnitude of the thermotransport. Values ranging from 6.6 to 7.2 kcal/mol were reported in zirconium,¹⁹⁾ 6.2 kcal/mol for Zircaloy-2 and 7 kcal/mol for Zircaloy-4.¹⁰⁾ The diffusivity of hydrogen in Zircaloy-2 has been determined by Sawatzky,¹⁸⁾ those in zirconium by Mallett and Albrecht¹⁴⁾ and by Someno²⁰⁾ and that in Zircaloy-4 by Kearns.¹¹⁾ The variability among these determinations was not exceptionally large and thus the data from Kearns was used for the calculations of Eqs. (2) and (3) in this study.

Fig. 3 shows the logarithmic plot of hydrogen concentration as a function of the inverse temperature in the single-phase region of modified Zircaloy-4 specimens. In this study, the value of Q^* was obtained by the least-square regression method. From Fig. 3(a), values of Q^* in Modified alloy-A with initial hydrogen concentrations of 63.3, 76.5 and 91.7 ppm were measured to be 6.8, 7.0 and 7.1 kcal/mol, respectively. The experimental data points in Fig. 3(a) deviate from the lines obtained by the least-squared regression by 21%. Considering the statistical error range, it is likely that Zircaloy and Modified alloy-A have the same value of Q^* of around 7 kcal/mol. It should be noted that the value of Q^* for hydrogen was not affected by

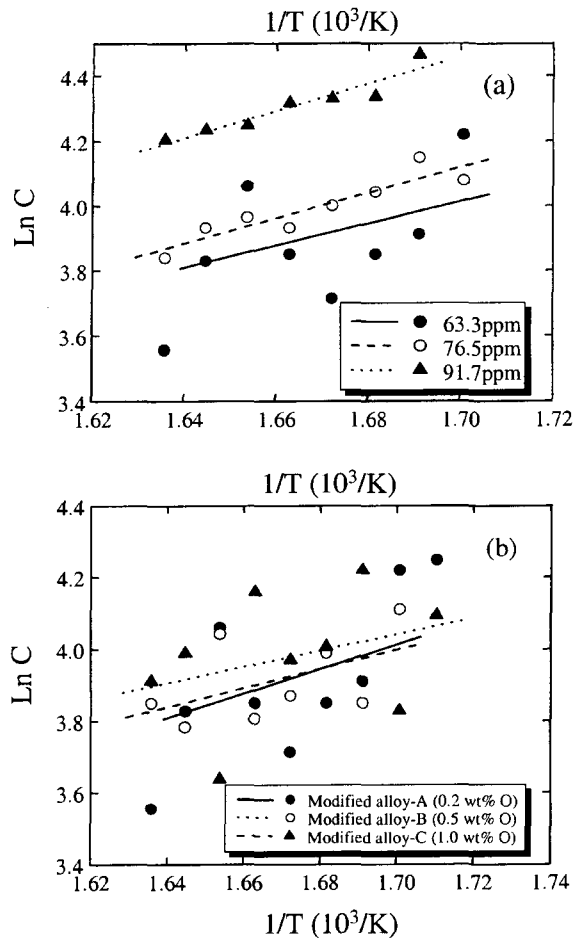


Fig. 3. Logarithmic plot of hydrogen concentration as a function of the inverse temperature. (a) Modified Zircaloy-4 as a function of hydrogen concentration (b) Modified Zircaloy-4 as a function of oxygen concentration.

the initial hydrogen concentration.

Fig. 3(b) shows the dependence of the heat of transport, Q^* , on the initial oxygen concentration in modified Zircaloy specimens (Modified alloy-A, -B and -C). It can be seen that Q^* values decreased from 6.8 to 5.3 and 4.5 kcal/mol as the initial oxygen concentration was increased from 0.2 to 0.5 and 1.0 wt%, respectively. This relationship was considered to be caused by the trapping of hydrogen by oxygen. Trapping of hydrogen by impurities is pronounced, especially by the interstitial element of O in Zr alloys.^{21,22)} Since hydrogen is trapped with a high binding energy, it is difficult for it to diffuse. Therefore, the value of Q^* was dependent on the oxygen content in the present specimens.

The schematic diagrams of the process of thermotransport in the present specimens are shown in Fig. 4. Fig. 4(a) illustrates that the initial hydrogen concentration is uniform and the concentration is higher than the terminal solubility in the colder region. N_s represents the terminal solubility line and C_1 the initial uniform hydrogen concentration. T_C

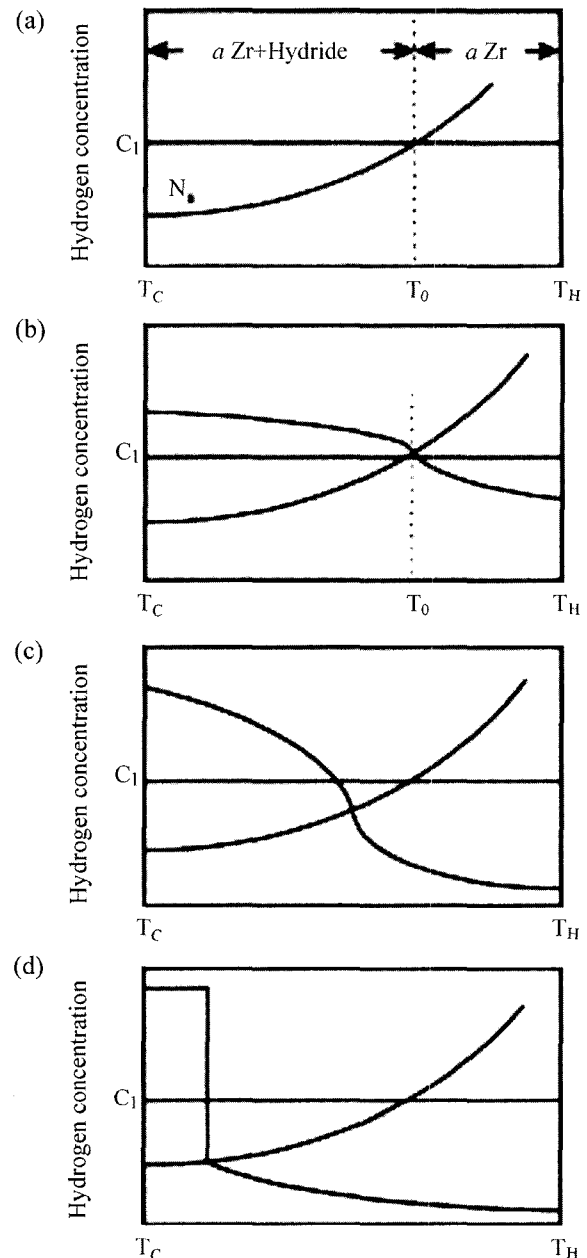


Fig. 4. Schematic diagram of hydrogen distribution: T_C and T_H are the temperatures at the cold and hot ends of the specimens. T_0 is the temperature at the initial position of the interface between the single-phase region and the two-phase region. (a) Initial uniform hydrogen distribution; (b) Hydrogen distribution sometime before steady state has been achieved; (c) Hydrogen distribution at intermediate stage; (d) Final hydrogen distribution at steady state.

and T_H are the temperatures at the cold and hot ends of the specimens. T_0 is the temperature at the initial position of the interface between the single-phase region and the two-phase region. When thermotransport of hydrogen begins in the solid solution, the gradient of concentration is established as shown in Fig. 4(b). The hydrogen moving away from the hot end region would tend to accumulate as hydride at the interface between the single-phase and the

two-phase region. As the thermotransport proceeds to a stage beyond a stage of Fig. 4(b), the hydride initially present at T_0 in Fig. 4(b) begins to dissociate and go into solid solution; as hydrogen in solid solution moves from the interface at T_0 to the colder region by the thermotransport, the hydrogen concentration in the solid solution at T_0 becomes lower than the solubility limit for the temperature of T_0 . The solid solution is assumed to be in equilibrium with the hydride at T_0 . Thus, the hydride would dissociate and go into solid solution to maintain an equilibrium at T_0 . The diffusion rate in the single-phase region is higher than in the two-phase region, so that a steady state hydrogen distribution will first be achieved in the single-phase region. As the thermotransport proceeds, the interface between the single-phase and the two-phase region moves toward the colder surface. Hydride precipitation and dissolution at the moving interface are repeated until the steady state is reached. Ultimately the hydride must precipitate at the cold end of the specimen through an intermediate stage of Fig. 4(c) as shown in Fig. 4(d). The schematic concentration profile in Fig. 4(c) is drawn from the result of the thermotransport test in Figs. 1 and 2.

4. Conclusion

Hydrogen in modified Zircaloy-4 specimens moved towards the colder regions as a result of thermotransport under a temperature gradient ranging from 300-340°C. Zirconium hydride was precipitated at the cold end of the specimens and the temperature at the interface between the single-phase and the two-phase region was in the range of 310-320°C. This interface temperature increased as the initial hydrogen concentration was increased but it was not affected by the initial oxygen concentration. Values for the heat of transport, Q^* , were around 7.0 kcal/mol for all samples. The value of Q^* was not influenced by the initial hydrogen concentration. However, the Q^* value for hydrogen

decreased from 6.8 to 4.5 kcal/mol as the oxygen concentration was increased from 0.2 wt % to 1.0 wt%. The decreased in the Q^* value for hydrogen was thought to be due to the trapping of hydrogen by oxygen.

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