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THE DIFFUSION AND SOLUBILITY OF HYDROGEN IN THE ALPHA-PHASE OF ZIRCALOY-2

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The diffusion of hydrogen in the alpha-phase of Zircaloy-2 was measured in the temperature range 260° to 560° C using the gradient technique. The diffusion coefficient was found to be

$$D = 2.17 \times 10^{-3} \exp(-8380/RT) \text{ cm}^2/\text{sec}.$$

The terminal solid solubility of hydrogen in Zircaloy-2 was determined in the temperature range 260° to 650° C using a modification of the gradient technique. The solubility is given by

$$C_0 = 8.50 \times 10^4 \exp(-7600/RT) \text{ ppm } H_2$$

by weight.

La diffusion de l'hydrogène dans la phase α du zircaloy-2 a été mesurée entre 260 et 560° C par la technique du gradient. Le coefficient de diffusion déterminé par cette méthode est

$$D = 2{,}17 \times 10^{-3} \exp(-8380/RT) \text{ cm}^2/\text{sec}.$$

La solubilité terminale dans l'état solide de l'hydrogène dans le zircaloy-2 a été déterminée entre 260° et 650° C en utilisant une variante de la technique du gradient. La solubilité est donnée par

$$C_0 = 8{,}50 \times 10^4 \exp(-7600/RT) \text{ ppm de } H_2$$

en poids.

Die Diffusion von Wasserstoff in der α-Phase von Zirkaloy-2 wurde im Temperaturbereich von 260° bis 560° C unter Anwendung der Gradientenmethode untersucht. Der Diffusionskoeffizient wurde zu

$$D = 2{,}17 \times 10^{-3} \exp(-8380/RT) \text{ cm}^2/\text{sec}$$

ermittelt.

Die maximale Löslichkeit von Wasserstoff in Zirkaloy-2 wurde zwischen 260° und 650° C bestimmt, wobei eine abgewandelte Form der Gradientenmethode verwendet wurde. Die Löslichkeit wird in Gew.-ppm gegeben durch

$$C_0 = 8{,}50 \times 10^4 \exp(-7600/RT).$$

1. Introduction

Zircaloy-2 has the properties of low corrosion rate, reasonable strength up to at least 300° C and low neutron absorption, all of which make it desirable as a structural material in water cooled power reactors. One of its chief disadvantages, however, is a drastic reduction in impact strength brought by about the presence of the hydride phase [1]). A knowledge of the hydrogen distribution and the terminal solid solubility is therefore necessary to predict the useful life of Zircaloy in the reactor.

As the Zircaloy-2 pressure tubes in the NPD (Nuclear Power Demonstration) reactor will operate at 260° C it was necessary to know the diffusion rate and the solubility limit of hydrogen in the α-phase of Zircaloy-2 at this temperature. Schwartz and Mallett [2]), Mallett and Albrecht [3]), and Gulbransen and Andrews [4]) measured the terminal solid solubility of hydrogen in zirconium, but only Mallett and Albrecht made measurements at temperatures as low as 305° C. Extrapolation of these data to 260° C gave terminal solid solubilities of 75, 45 and 28 parts per million (ppm) by weight respectively. Since the last value is similar to the amount of hydrogen normally present in Zircaloy-2 tubing, it was important to establish the terminal solid solubility of hydrogen in Zircaloy-2 at 260° C.

Although the degassing method employed by Eborall and Ransley [6]) for determining the diffusion of hydrogen in an Al-Mg alloy was tried, it was decided that the technique used by Mallett and Albrecht [3]) for measuring the diffusion of hydrogen in zirconium would give more reliable results in the temperature range of interest. Essentially, the method consists of

determining the hydrogen distribution in a Zircaloy cylinder annealed in hydrogen for a predetermined time.

The diffusion experiment yielded values of terminal solid solubility, but more accurate results were obtained by a modification of this technique. A thin hydride film was formed on a Zircaloy cylinder by reaction with hydrogen and annealed for a time sufficient to homogenize the alpha phase. Hydrogen analysis then gave the terminal solid solubility directly.

2. Experimental Procedure

2.1. Material

The two sources of Zircaloy-2 with compositions given in table 1 were in the form of rods swaged to 0.5 in. diameter. Micrographic examination showed that the FZ-644 batch was in the as-swaged conditions, whereas the K-28 material had been annealed in the alpha region.

Table 1
Analysis of the Zircaloy-2
Alloy analysis in wt percent

Element	Ingot FZ-644	Ingot K-28
Sn	1.36	1.51
Fe	0.13	0.15
Cr	0.10	0.10
Ni	0.05	0.05
Impurities in ppm by wt		
N	35	31
C	90	< 300
Si	77	30
Al	38	21
Hf	< 100	72
Cu	< 25	< 20
V	< 25	< 20
Mn	35	< 20
Mg	< 10	< 20
Pb	< 20	< 20
Mo	< 20	< 20
Co	< 10	< 20
W	< 21	< 20
B	< 0.3	< 0.2
Cd	< 0.2	< 0.5
O	< 1200	< 1400
H	45	32

2.2. Apparatus

A schematic diagram of the apparatus is shown in fig. 1. Except for several modifications, it is the hot-extraction apparatus described by McGeary [5]).

The sample furnace consisted of nichrome ribbon wound on a Vycor tybe, and was capable of reaching temperatures up to 1100° C. The manual temperature control using a Variac produced variations of less than ± 1° C. The working zone of the furnace had a maximum temperature variation of 3° C over 1.5 inches. A chromel-alumel thermocouple made from National Bureau of Standards calibrated wire was placed against the bottom of the sample-tube and calibrated to read sample temperature. The error in specimen temperature was approximately ± 5° C.

Each of the two high-speed mercury diffusion pumps 1 and 2 had a large cold trap sealed to the high vacuum outlet. Pump No. 1, used to transfer the hydrogen from the sample tube into the analysis volume, attained a pressure of less than 0.01 microns with a back pressure of 1500 microns.

The total analysis volume consisted of the 1050-cc flask, the 2000-cc flask, the McLeod gauge, the tubing and the low vacuum side of pump No. 1. This volume was calibrated by introducing hydrogen into the analysis volume and measuring the pressure with the McLeod gauge. The 1050-cc flask, whose volume had been accurately determined before assembly, was then evacuated and the hydrogen contained in the rest of the volume expanded into it. By measuring the final pressure and applying the perfect gas law the total volume was calculated. Suitable combinations of the two flasks A and B (fig. 1) together with the associated tubing between diffusion pump No. 1 and the McLeod gauge enabled one to have four different analytical volumes.

The palladium valve used to introduce pure hydrogen into the system was a spiral of palladium tubing with a 0.064 cm wall, 0.32 cm diameter and 30 cm length. One end of this

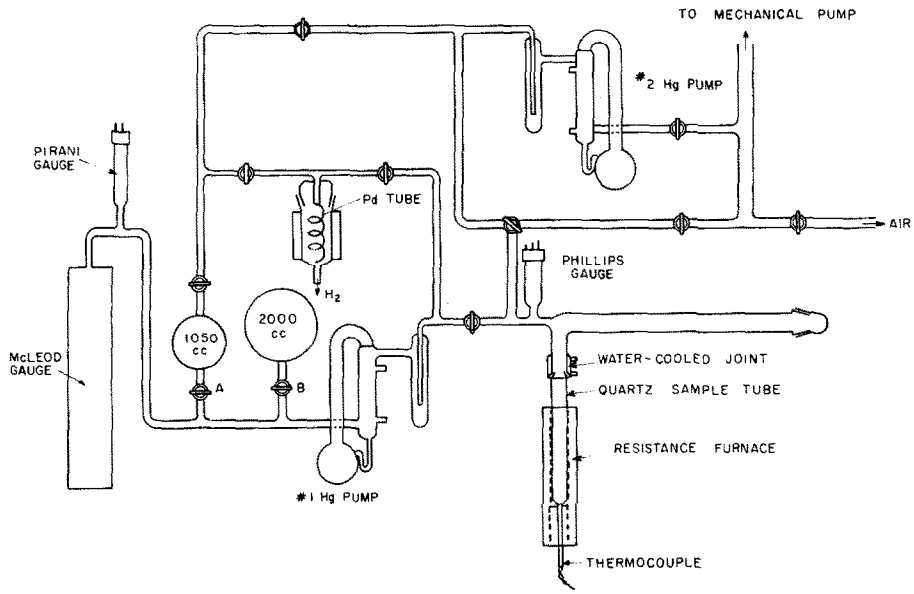


Fig. 1. Hot extraction apparatus for hydrogen analysis.

spiral was silver-soldered to the Kovar tip joined to a short length of glass tubing, and the other end was closed. With the palladium tube at 400° C a hydrogen pressure of 100 mm in the system could be attained in one hour.

2.3. The diffusion experiment

A Zircaloy cylinder 1 cm in diameter and 3 cm long was degassed in vacuum for six hours at 830° C. A residual hydrogen concentration of 5 to 6 ppm by weight as determined from the equilibrium curves, remained in the specimen after this treatment. The sample was abraded with 600-A grit carbide paper and placed in the sample tube of the furnace. It was then heated in vacuo for 0.5 h at 830° C to remove any oxide film and brought to the diffusion temperature. Hydrogen, at a pressure of 200 mm was next introduced into the sample tube; this pressure was sufficient to maintain a hydride film on the specimen surface. The sample was kept at the diffusion temperature for a sufficient time to give a suitable hydrogen distribution, after which the furnace was quickly removed and the sample tube quenched in liquid nitrogen. Lengths equal to the diameter were removed from the end of each sample in order to eliminate effects due to the finite specimen length. The remaining portion was machined into seven layers of equal weight. The outer layer containing the hydride was discarded and the remaining six analysed for hydrogen.

A plot of concentration versus radius when extrapolated to the sample surface gave the terminal solid solubility C_0. The diffusion coefficient was determined from the plot of $(C-C_1)/(C_0-C_1)$ versus r/a where:

C = Hydrogen concentration at radius r

C_1 = Initial uniform hydrogen concentration

C_0 = Surface concentration of hydrogen in the α-Zr phase

a = radius of sample.

2.4. Determination of the terminal solid solubility

Since the terminal solid solubilities obtained by the above method are susceptible to fairly large errors due to extrapolation, a variation of this technique leading to more accurate results was also used.

The Zircaloy used in these measurements was cold-worked 40 % to eliminate possible effects due to differences in the microstructure of the two batches of material. The specimens were 2 cm in length and 0.5 cm in diameter except

for those treated at 260° C which were 0.4 cm in diameter.

Two samples, one from each batch, were placed together in the furnace and given the same degassing and oxide-removal treatment as the diffusion specimens. With the samples at the desired temperature, hydrogen at a pressure of 150 mm was introduced into the sample tube. After the samples had absorbed enough hydrogen to form a hydride skin approximately 0.005 cm thick, the pressure was reduced to a value [7]) which was just sufficient to maintain the hydride film without causing further growth. The samples were held at the diffusion temperature for a time $t=a^2/D$ where D is the diffusion coefficient at operating temperature. This time was long enough to give a uniform hydrogen distribution in the alpha phase to within 1 %. Sample dimensions had been chosen to allow homogenization in reasonable times. After removal from the furnace a layer 1 mm thick was machined from the specimen surface to remove the hydride film, and the remaining portion analysed for hydrogen. The resultant concentration was the terminal solid solubility.

2.5. Analysis of the diffusion data

Since the technique used results in effectively radial diffusion, the diffusion equation becomes:

$$\frac{\partial c}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) \qquad (1)$$

where c – concentration

t – time

r – radius

D – diffusion coefficient.

This equation must be solved using the following boundary conditions:

1) $c=C_0$ at $r=a$ for $t \geqslant 0$

2) $c=C_1$ for $0<r<a$ at $t=0$.

As shown in Crank [8]) the solution to eq. (1) is

$$\frac{C-C_1}{C_0-C_1} = 1-\frac{2}{a}\sum_{n=1}^{\infty}\exp\left(-D\alpha_n^2 t\right)\frac{J_0(r\alpha_n)}{J_1(a\alpha_n)} \qquad (2)$$

where $J_0(x)$ and $J_1(x)$ are first-kind Bessel functions of zero and first order respectively, and the α_n's are the positive roots of $J_0(a\alpha_n)=0$. The solution to eq. (2) can be written in terms of the two dimensionless parameters Dt/a^2 and r/a. Curves showing $(C-C_1)/(C_0-C_1)$ as a function of r/a for different values of Dt/a^2 may be found in Crank's book.

In practice the experimental values of $(C-C_1)/(C_0-C_1)$ are plotted against r/a and compared with the theoretical curves. A value for Dt/a^2 is thus obtained and, since t and a are known, D can be calculated. The experimental conditions are chosen so that a thin hydride film is formed on the sample. The hydrogen concentration in the Zircaloy that is in equilibrium with the hydride, namely the terminal solid solubility, is then C_0 in the above equation.

3. Results and Discussions

3.1. Diffusion coefficients

The diffusion of hydrogen in the alpha-phase of Zircaloy-2 was investigated in the range 260° to 560° C. The plot of $(C-C_1)/(C_0-C_1)$ against r/a for 358° C, which is typical of the curves obtained, is shown in fig. 2. The points are the experimental values and the line is the best theoretical fit from which D was determined. Scatter for small values of $(C-C_1)/(C_0-C_1)$ as observed in most of the curves is to be expected since the relative error increases as C approaches C_1.

Table 2

Diffusion of hydrogen in Zircaloy-2

Temp. (° C)	Time (min)	Batch No.	$D \times 10^6$ (cm²/sec⁻¹)	C_0 (ppm by wt) uncorr.	C_0 (ppm by wt) corr.
261	150	K-28	0.80	75	71
315	90	K-28	1.70	115	105
358	60	K-28	2.94	300	280
408	30	FZ-644	4.71	180	145
458	15	FZ-644	5.49	490	450
515	15	K-28	10.3	800	700
560	15	K-28	15.8	—	—

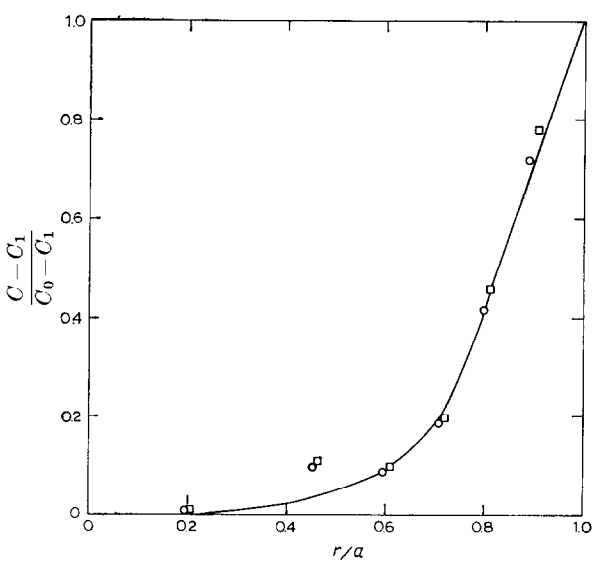
The diffusion coefficients obtained at the various temperatures are tabulated in table 2. The values of C_0 obtained by extrapolating the

concentration curves to the sample surfaces are also given.

The assumption is usually made [3]) that the hydride film is negligibly thin. Using the data of Gulbransen and Andrew [9]) for the diffusion of hydrogen in zirconium hydride, the hydride thickness was determined, and a value for C_0 found by extrapolating the concentration curve only to the hydride boundary. As shown in table 2 the correction was appreciable. These corrected values fell reasonably close to the C_0's obtained by the second method used, except for the point at 408° C. The uneven hydriding of this specimen may explain the very low value for C_0. A corrected D was obtained using the corrected C_0 and assuming the average specimen radius to be midway between the specimen surface and the hydride boundary. The correction here was found to be negligible as shown in fig. 2.

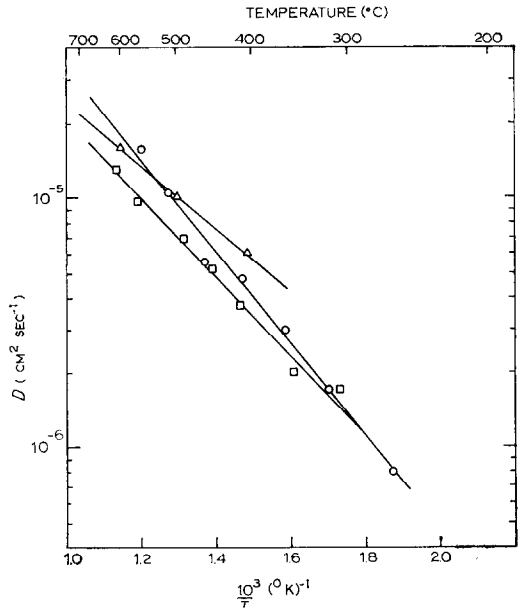
The logarithm of D versus $1/T$ is plotted in fig. 3. A least-squares fit of the experimental data gives an activation energy $Q = 8380 \pm 400$ cal/mole and a diffusion coefficient

$$D = 2.7 \times 10^{-3} \exp(-8380/RT) \text{ cm}^2/\text{sec}.$$



○ Uncorrected.
□ Corrected.
Temperature 358° C.

Fig. 2. Normalized hydrogen concentration against radius.



○ Present work.
△ Schwartz and Mallett.
□ Mallett and Albrecht.

Fig. 3. Comparison of diffusivities.

In the same figure the present data are compared with those of Schwartz and Mallett [2]) and Mallett and Albrecht [3]) for the diffusion of hydrogen in zirconium. Although the diffusivities at any one temperature are quite similar in the three cases, the activation energy obtained in the present investigation (8380 cal/mole) is somewhat higher than those of either Schwartz and Mallett (5700 cal/mole) or Mallett and Albrecht (7060 cal/mole). It should be noted that Schwartz and Mallett's result is based on only three measurements. The two different activation energies obtained for hydrogen diffusion in zirconium are possibly due to different amounts of impurities such as oxygen or nitrogen in the zirconium used. Zircaloy-2 contains the four alloying elements shown in table 1, which undoubtedly contribute to the difference in activation energy between hydrogen diffusion in zirconium and Zircaloy-2.

3.2. Terminal solid solubilities

Terminal solid solubilities were measured in the range 260° to 650° C by the second method described earlier. Table 3 lists the solubilities

TABLE 3

Terminal solid solubilities for H in Zircaloy-2

Temp. (° C)	Time (hours)	C_0 (ppm by wt) FZ-644	C_0 (ppm by wt) K-28	C_0 (average)
257	20	79	81	
257	18	76	50	71
300	11	93	95	
300	11		87	
300	12	99	101	95
356	11	212	218	
356	13	189	191	203
406	4	273	268	270
460	3.5	478	468	
457	7	480	465	473
500	4	635	640	638
560	4	888	886	887
600	2	3075		3075
650	2	3200	3170	3185

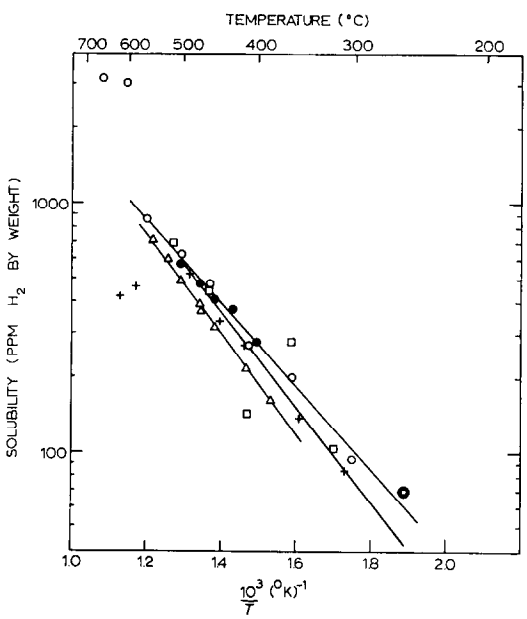
obtained for the two batches of Zircaloy tested. In general the reproducibility is quite good, and it was also found that the terminal solid solubility for the two materials is essentially the same.

The logarithm of C_0 versus $1/T$ is plotted in fig. 4. A least-squares fit of the experimental data yields

$\Delta_H = 7600 \pm 200$ cal/mole and

$C_0 = 8.50 \times 10^4 \exp(-7600/RT)$ ppm H_2 by weight.

Δ_H represents the difference in partial molar heats of solution of hydrogen in the δ(hydride) and α phases. The least-squares value of the solubility at 260° C is 64 ppm whereas the average of four determinations at 257° C is 71 ppm.



+ Mallett and Albrecht.
△ Gulbransen and Andrew
● Schwartz and Mallett.
□ Present work, diffusion method 1.
○ Present work, method 2.

Fig. 4. Comparison of terminal solid solubilities.

In fig. 4, the solubility of hydrogen in Zircaloy-2 found in the present investigation is compared with the published values for the solubility of hydrogen in zirconium. The data of Schwartz and Mallett [2]), Mallett and Albrecht [3]) and Gulbransen and Andrew [4]) extrapolated to 260° C lead to terminal solid solubilities of 75, 45 and 28 ppm H_2 by weight respectively. Although the present solubility of hydrogen in Zircaloy-2 (64 ppm) agrees best with that of Schwartz and Mallett, the latter covered only the temperature range 400° to 500° C making extrapolation to 260° C rather unreliable. However, on the basis of probable errors in the hydrogen analyses and temperatures, the present solubilities are accurate to within ± 10 %.

It will be seen that at 600° C and 650° C the results fall off the straight line shown in fig. 4. Metallographic examination of these two samples showed that they had been annealed in the beta region. This shows that the α-phase was not in equilibrium with the δ-phase at these temperatures, in agreement with the equilibrium diagram of Ells and McQuillan [7]).

On the basis of this diagram, in a diffusion experiment carried out between 560° to 850° C, one should get a hydride (δ-phase) layer on the specimen surface, followed by a layer of β (bcc) phase, the rest of the specimen being α (hcp) phase. If the annealing was carried out for a long time, the α-phase region would gradually give away to the β-phase. The specimens corresponding to the points at 600° C and 650° C in fig. 4 were annealed for two hours, which left the major portion of these specimens

in the β-phase, thus accounting for the observed higher hydrogen concentrations. In contrast, the two samples at 600° C and 650° C studied by Mallett and Albrecht were annealed for approximately five minutes. The major portion of their samples would be in the α-region, giving values of C_0 nearly equal to the terminal solubility at 560° C. As seen in fig. 4, their values for C_0 at temperatures above 560° C are slightly lower than expected according to Ells and McQuillan.

4. Conclusions

The diffusion coefficient of hydrogen in Zircaloy-2 is

$$D = 2.17 \times 10^{-3} \exp(-8380/RT) \text{ cm}^2/\text{sec}.$$

The terminal solid solubility of hydrogen in Zircaloy-2 is

$$C_0 = 8.50 \times 10^4 \exp(-7600/RT) \text{ ppm } H_2$$

by weight.

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