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HYDROGEN IN ZIRCALOY-2: ITS DISTRIBUTION AND HEAT OF TRANSPORT

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Two determinations of the heat of transport for hydrogen in zircaloy-2 have been made under steady-state conditions over the temperature range 300° to 500° C. Values of 4.7 and 6.1 kcal/mole were obtained.

Similar experiments on deuterium gave values of 6.2 and 6.8 kcal/mole.

An equation has been developed giving the hydrogen concentration in the two-phase (alpha plus hydride) region as a function of time and temperature. On the basis of this equation, a model for the over-all hydrogen distribution under the influence of a temperature gradient is proposed. The model has been fitted to several experimental curves and the agreement found to be very good. The model predicts that for hydrogen pickup on the hot surface (as in a failure of a fuel-rod sheath) maximum hydriding will occur at some position displaced from the cold surface. This prediction is supported by observations made on a failed zircaloy-2-clad UO_2 fuel element.

Deux déterminations de la chaleur de transport pour l'hydrogène dans le zircaloy-2 ont été effectuées dans l'intervalle de températures 300–500° C dans des conditions de régime permanent. Les valeurs de 4,7 et 6,1 kcal/mole ont été trouvées.

Des expériences similaires avec le deutérium donnèrent des valeurs de 6,2 et 6,8 kcal/mole.

Une équation a été déterminée reliant la concentration en hydrogène dans le domaine biphasé (α + hydrure) au temps et à la température. En se basant sur cette équation, on propose un modèle représentant la distribution de l'hydrogène total sous l'influence d'un gradient de température. Le modèle a été appliqué à plusieurs courbes expérimentales et l'accord trouvé très satisfaisant. Ce modèle prédit que dans le cas de l'absorption d'hydrogène sur une surface chaude (cas de la rupture d'une gaine) l'hydruration maximum se produira dans une position déplacée vis-à-vis de la surface froide. Cette prévision est confirmée par les observations faites sur des ruptures de gaine d'éléments combustibles UO_2 gainés au zircaloy-2.

Im Temperaturbereich von 300 bis 500° C wurden zwei Bestimmungen der Transportwärme von Wasserstoff in Zircaloy-2 durchgeführt, wobei Werte von 4,7 und 6,1 kcal/mol erhalten wurden. Gleichartige Messungen an Deuterium ergaben Werte von 6,2 und 6,8 kcal/mol.

Eine abgeleitete Gleichung gibt den Zusammenhang zwischen der Wasserstoffkonzentration im Zweiphasenbereich (α + Hydrid) und Temperatur und Zeit an. Hiervon ausgehend wird ein Modell für die gesamte Wasserstoffverteilung unter dem Einfluss eines Temperaturgradienten entwickelt. Das Modell wurde verschiedenen Messkurven angepasst, wobei sich eine sehr gute Übereinstimmung erzielen liess. Nach diesem Modell liegt bei Aufnahme von Wasserstoff an einer heissen Oberfläche (etwa an einer Schadenstelle in der Hülle eines Brennelements) die höchste Wasserstoffkonzentration in einigem Abstand von der kalten Oberfläche vor. Diese Voraussage wird durch Beobachtungen gestützt, welche an UO_2-Brennelementen mit beschädigten Hüllen aus Zircaloy-2 zu machen waren.

1. Introduction

One of the problems associated with the use of zircaloy-2-clad UO_2 fuel elements in pressurized-water power reactors is that zircaloy-2 picks up hydrogen during operation. Because precipitates of zirconium hydride in zircaloy-2 can have pronounced effects on the mechanical properties it is important to know how the hydrogen redistributes itself during operation.

It has been shown [1]) that under the influence of a temperature gradient, hydrogen in zircaloy-2 will tend to move to the colder regions until a steady-state distribution, determined by the so-called heat of transport, is attained. Shew-

mon [2]) has qualitatively discussed thermal diffusion and arrived at an expression for the hydrogen current in the two-phase region. From this he was able to calculate the time to steady state. The hydrogen distribution as a function of time and position, however, has never been carefully considered.

In the present investigation the heat of transport for both hydrogen and deuterium has been determined. An expression for the hydrogen distribution has been developed and applied to several experimental curves. The practical case of hydrogen pickup at a hot surface, as in a fuel-sheath failure, is treated mathematically and the result used to explain the hydride distribution found in an actual sheath failure.

2. The Distribution Equation

The model used for thermal diffusion in the two-phase region is basically the one proposed by Shewmon [2]). The assumptions made are as follows:

1. Hydrogen is the only component diffusing.
2. The hydride is in equilibrium with the solid solution at every point in the two-phase region. As the diffusing current increases, this assumption becomes less reliable.
3. Diffusion is predominantly in the solid-solution (alpha) phase. This implies a large ratio of hydrogen diffusivity in the alpha phase to that in the hydride as well as a small ratio of hydride volume to alpha-phase volume.

With these assumptions, thermal diffusion in the two-phase region can be treated as diffusion in the single phase with the concentration fixed at each point, the hydride serving merely as a source or sink for hydrogen.

In the presence of a temperature gradient the atomic diffusion flux in the single-phase region J, is given by Denbigh [3]) as

$$J = \frac{-DN}{RT}\left\{RT\,\frac{\mathrm{d}\ln N}{\mathrm{d}x} + \frac{Q^*}{T}\,\frac{\mathrm{d}T}{\mathrm{d}X}\right\} \tag{1}$$

where D is the diffusion coefficient, N the hydrogen concentration, T the temperature in °K, R the gas constant, and Q^* the heat of transport.

Since the solid solution at every point in the two-phase region is assumed to be in equilibrium with the hydride at the corresponding temperature

$$N = N_s = N_0 \exp\left(-\Delta H/RT\right) \tag{2}$$

where N_s is the terminal solid solubility, N_0 a constant, and ΔH the heat of mixing.

Substituting (2) into (1) leads to

$$J = \frac{-DN_s}{RT^2}\left(\Delta H + Q^*\right)\frac{\mathrm{d}T}{\mathrm{d}x} \tag{3}$$

the flux equation originally obtained by Shewmon [2]).

The diffusion coefficient is given by the Arrhenius-type expression

$$D = D_0 \exp\left(-Q/RT\right) \tag{4}$$

where D_0 is the frequency factor and Q the activation energy for diffusion.

For the case of a constant temperature gradient

$$\mathrm{d}T/\mathrm{d}x = K. \tag{5}$$

Eqs. (2), (4) and (5) substituted in (3) lead to

$$J = \frac{-D_0 N_0 K}{RT^2}\left(\Delta H + Q^*\right)\exp - \left(\frac{\Delta H + Q}{RT}\right). \tag{6}$$

In one-dimensional flow, which is considered here, the continuity equation is given by

$$\frac{\partial N}{\partial t} = \frac{-\partial J}{\partial x} = \frac{-K\partial J}{\partial T} \tag{7}$$

where $\partial N/\partial t$ is the variation with time of the total hydrogen concentration at point x. Since the hydrogen concentration in the solid solution is independent of time, $\partial N/\partial t$ is the rate of change of the hydride concentration.

Differentiating (6) with respect to T and substituting into (7) leads to

$$\left.\begin{aligned}\frac{\partial N}{\partial t} = \frac{K^2 D_0 N_0 (\Delta H + Q^*)}{RT^4}\,\cdot \\ \cdot\left(\frac{\Delta H + Q)}{R} - 2T\right)\exp - \left(\frac{\Delta H + Q}{RT}\right)\end{aligned}\right\} \tag{8}$$

which on integration becomes

$$\left.\begin{aligned}N - N_I = \frac{K^2 D_0 N_0 (\Delta H + Q^*)}{RT^4}\,\cdot \\ \cdot\left(\frac{\Delta H + Q}{R} - 2T\right)\cdot t\cdot \exp - \left(\frac{\Delta H + Q}{RT}\right)\end{aligned}\right\} \tag{9}$$

where N_I is the initial hydrogen concentration.

3. Hydrogen Redistribution

3.1. No hydrogen pickup

If hydrogen is uniformly distributed throughout the material and a temperature gradient applied such that the hydrogen concentration over at least part of the system is greater than terminal solid solubility, the initial situation is represented by fig. 1*a*. The temperatures at the cold and hot surfaces are T_C and T_H respectively. T_0 is the temperature at the initial position of the interface between the single-phase region and the two-phase region (hereafter simply stated as interface). N_I is the initial uniform hydrogen concentration and N_S the terminal solid solubility, so that the hydride concentration is given by the shaded area.

According to eq. (9) the hydride concentration at any point within the two-phase region increases linearly with time, the rate of hydriding being greater the higher the temperature. Singularities in J exist at the cold surface and at the interface as shown by the discontinuities in the alpha-phase concentration gradient at these points. Eq. (9) therefore does not apply at these points and a separate treatment must be given.

The hydrogen flow into the cold surface is given by $J(T_C)$ in (6). Since no hydrogen leaves the surface a layer of zirconium hydride is formed, whose thickness is given by

$$X = \frac{J(T_C)\cdot t}{N_H} \tag{10}$$

where N_H is the hydrogen concentration in zirconium hydride.

The time to steady state is given approximately as the time required for all the hydrogen to be precipitated out as hydride at the cold surface, namely

$$t_E = \frac{N_I \cdot l}{J(T_C)} \tag{11}$$

where l is the thickness of the specimen. This is the limiting case of the more general expression due to Shewmon [2]).

The diffusion rate is greater the higher the temperature, so that in the single-phase region a "near" steady state hydrogen distribution will first be achieved in the hotter regions. To conserve hydrogen a maximum in hydrogen concentration must be built up somewhere in the single-phase region. The position of the maximum will determine the slope of the single-phase hydrogen distribution at the interface. This slope can be either less or slightly greater than the slope of the terminal solid solubility curve at this point.

Since hydrogen is conserved, the application of equation (1) to both sides of the interface will indicate the direction in which the interface moves. It can move either towards the hot or cold surface depending on whether the hydrogen concentration gradient in the single-phase region is greater or less than that in the alpha phase of the two-phase region.

On the basis of the preceding discussion the interface initially moves toward the colder surface. As hydrogen redistribution in the

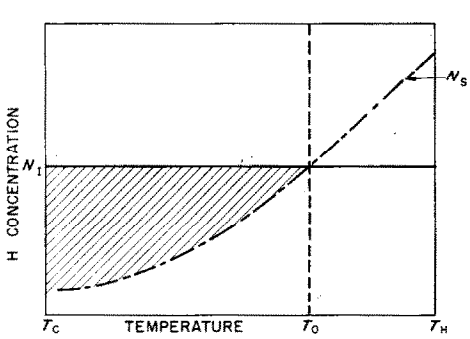

Fig. 1*a*. Initial hydrogen distribution, showing single-phase and two-phase regions.

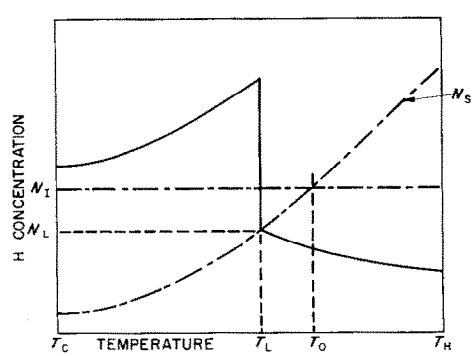

Fig. 1*b*. Hydrogen distribution sometime before steady state has been achieved.

single-phase region proceeds the hydrogen concentration peak moves toward the interface. This could lead to, although not necessarily, an interface movement toward the hotter surface. Eventually, however, as the concentration maximum disappears at the interface, the latter must again move towards the colder surface.

Since every point in the two-phase region gains hydrogen at a constant rate and the hydrogen concentration in the single-phase region at the interface decreases as it moves toward the colder surface, a sharp discontinuity in concentration will result as shown in fig. 1*b*.

The diffusion coefficient at every point in the single-phase region is higher than at any point in the two-phase region so that one might expect near steady-state conditions to exist in the single-phase region before the interface reaches the colder surface. The hydrogen distribution in the single-phase area may then be obtained by setting $J=0$ in eq. (1) and integrating. This leads to

$$N=C_0 \exp \frac{Q^*}{RT} \tag{12}$$

where C_0 a constant.

3.2. Hydrogen pickup at the cold surface

For the case under consideration, namely a two-phase region over part of the system, hydrogen pickup at the cold surface, as in a fuel sheath during normal reactor operation, will lead to a more rapid growth of the surface hydride layer. It will not, however, affect the distribution in either the single- or two-phase regions.

3.3. Hydrogen pickup at the hot surface

Hydrogen pickup at the hot surface, as in the case of a defected fuel-rod sheath, will in general result in a decrease of the rate at which the interface moves to the cold surface. It may be shown, however, that for a range of rate of hydrogen pickup the interface will remain fixed in position. If the interface is fixed and J_0 is the hydrogen current, constant throughout the single-phase region, then (6) leads to

$$J_0=\frac{-D_0N_0K(\Delta H+Q^*)}{RT_L^2}\exp-\left(\frac{\Delta H+Q}{RT_L}\right). \tag{13}$$

J_0 must have a value such that in the above equation $T_C<T_L<T_H$. It may also be seen from (13) that for a given temperature gradient the interface is found closer to the hot surface as J_0 increases.

4. Experimental Technique

The thermal diffusion specimens were cylinders of reactor grade zircaloy-2, 1.2 cm in diameter and 2.5 cm in length. Hydrogen was introduced into the specimen by heating at 900° C in a closed system containing the required amount of hydrogen. A six hour anneal led to a homogeneous hydrogen distribution. The specimen was removed from the system and heated in air for several minutes to form an oxide layer relatively impermeable to hydrogen. It was then bolted into position between a stainless steel cylinder and a brass plate. The stainless steel cylinder was heated in a nichrome wound tube furnace and served as heat source for the specimen. The brass plate had brazed to it on the side opposite to the specimen, a brass rod coaxial to the latter. A watercooled coil could be slid along the rod permitting the cold-end temperature of the specimen to be adjusted to the desired value. Glass wool was wrapped around the specimen to reduce heat losses through the surface. The temperatures at each end of the specimen were continuously monitored and showed a maximum variation of $\pm$ 3° C. A preliminary run with five chromel-alumel thermocouples equally spaced along the specimen indicated a constant temperature gradient.

After sufficient time (several weeks) at temperature to give the desired hydrogen distribution, the specimen was removed and cut into discs 0.1 cm thick. These were analyzed for hydrogen by the hot-extraction method, and the hydrogen distribution determined.

5. Experimental Results

Two thermal-diffusion runs were made to determine the heat of transport for hydrogen in zircaloy-2. The hot and cold ends of the specimens were held at 500° and 300° C. An initial uniform hydrogen concentration of 60 ppm by weight left the specimens completely in the solid solution (alpha) phase. Each experiment was continued for 44 days, this being calculated as sufficient time to arrive at the steady-state hydrogen distribution. The data for the two runs are plotted in fig. 2.

According to eq. (1), for $J=0$ (i.e. steady state)

$$\frac{d \ln N}{d(1/T)} = \frac{Q^*}{R}. \tag{14}$$

Values for Q^* of 4.7 and 6.1 kcal/mole were obtained from the slopes of curves A and B respectively, using the method of least squares.

The heat of transport for deuterium in zircaloy-2 was also measured. Two 62-day runs were made on specimens having an initial deuterium concentration of approximately 120 ppm by weight. The hot and cold ends of the specimen were held at 460° and 300° C. The data for the two runs are plotted in fig. 3. Values for Q^* of 6.2 and 6.8 kcal/mole were obtained from the slopes of curves C and D.

The scatter in curve B fig. 2, is believed to be due to the fact that the oxide skin was left on the specimen during hydrogen analysis. A comparison of the total hydrogen present in the specimen before and after the thermal diffusion anneal, showed that a small amount of hydrogen (about 2 percent of the initial concentration) had been picked up. Based on uncertainties in concentration, temperature, and thermocouple position, an observational error in the heat of transport of $\pm$ 15 % is considered a reasonable estimate.

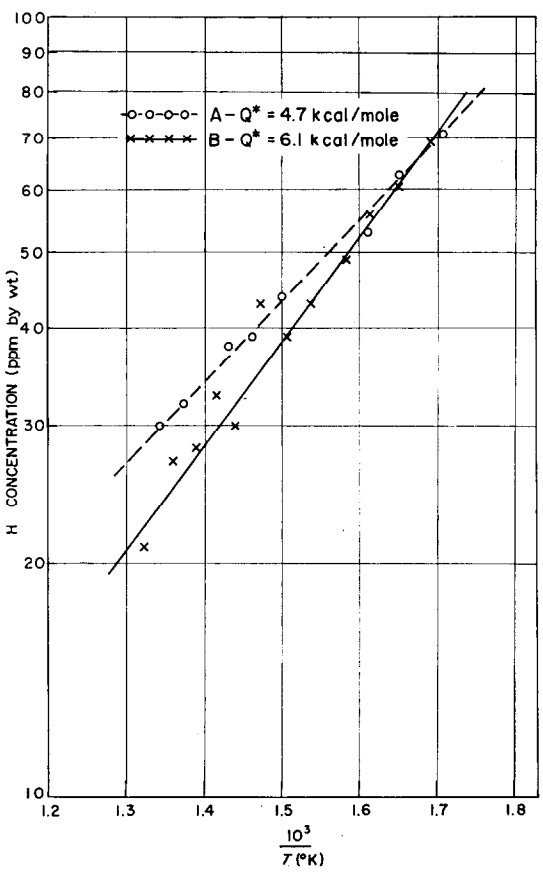

Fig. 2. Ln hydrogen concentration vs $1/T$.

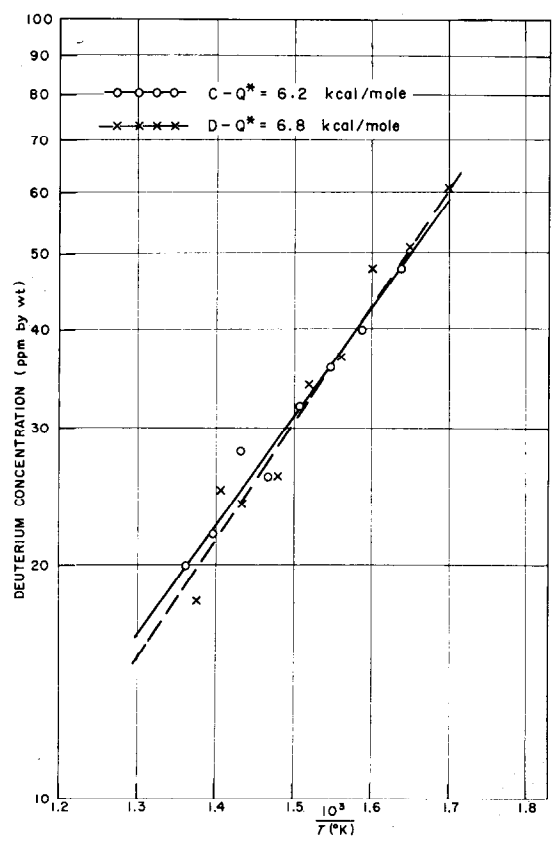

Fig. 3. Ln deuterium concentration vs $1/T$.

Two further thermal-diffusion runs for hydrogen in zircaloy-2 were made for times too short to allow the hydrogen to reach a steady-state distribution. One specimen, having an initial uniform hydrogen concentration of 130 ppm by weight, had hot and cold ends at 477° and 130° C. The points in fig. 4 give the experimental hydrogen distribution after a 34-day anneal. The other specimen had an initial hydrogen concentration of 64 ppm with hot and cold ends at 454° and 157° C. The hydrogen distribution after a 41-day anneal is given by the points in fig. 5. A heat of transport of 4.3 and 3.8 kcal/mole was estimated from the single-phase regions of figs. 4 and 5 respectively.

6. Discussion of the Results

The heat of transport for hydrogen in zircaloy-2, as obtained in the present investigation, varies between 3.8 and 6.1 kcal/mole. Values ranging from 1.6 to 6.5 kcal/mole have been reported by Markowitz [4]) and a value of 6.4 kcal/mole has been reported by Johnston *et al.*[5]). The range of values found in the present work and in that of Markowitz [4]) is greater than

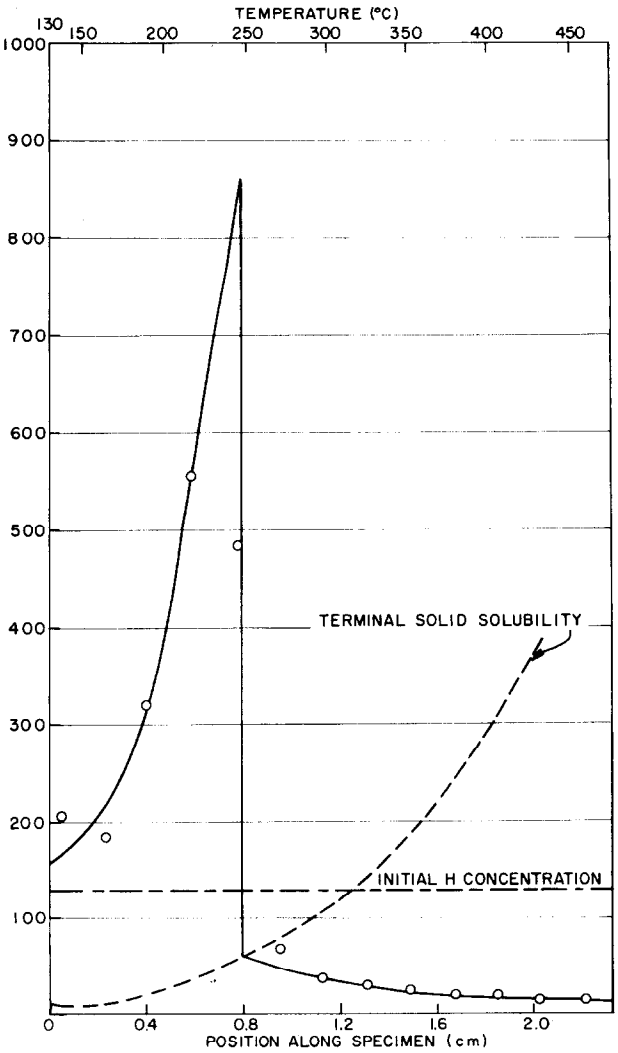

Fig. 4. Hydrogen distribution in zircaloy-2 after a 34-day anneal under a temperature difference 130°–477° C.

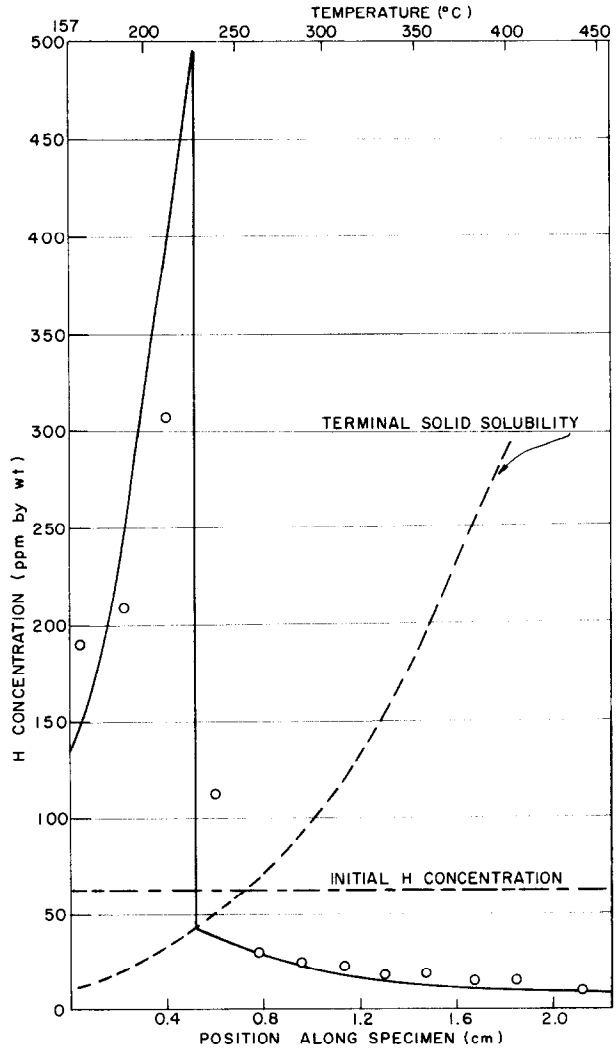

Fig. 5. Hydrogen distribution in zircaloy-2 after a 41-day anneal under a temperature difference 157°–454° C.

that which could be attributed to errors in measurement alone. It is suggested that a large contributing factor to the spread in values is insufficient time at temperature to arrive at the steady-state hydrogen distribution. This contention is supported by the fact that the short anneals (figs. 4 and 5) led to lower values for the heat of transport than long anneals (fig. 2). Hydrogen pickup during the experiment could also lead to a hydrogen distribution different from that of the true steady-state distribution. Both of these effects would in general result in an apparent Q^* smaller than the true value. It may be significant that the maximum values for the heat of transport obtained in the three independent investigations (6.1, 6.4 and 6.5 kcal/mole) fall well within the experimental error. On the basis of the foregoing, it is therefore felt that the heat of transport for hydrogen in zircaloy-2 is about 6.0 kcal/mole.

The heat of transport for deuterium in zircaloy-2, taken as the average of the two results from fig. 3, is 6.5 kcal/mole. Since the activation energies for the diffusion of hydrogen and deuterium are equal [6]), one might expect the heats of transport to be the same; this seems to be the case. Because of experimental error, however, differences of less than about 20 % in the heats of transport would not be detected.

In figs. 4 and 5 the experimental hydrogen distributions are compared with the theoretical ones as obtained from eqs. (9) and (12). The experimental hydrogen concentration is given by the points, the theoretical distribution by the solid line, and the terminal solid solubility by the dotted curve. The theoretical hydrogen distribution in the two-phase region was determined from eq. (9) using $D_0 = 2.17 \times 10^{-3}$ cm²/sec; $N_0 = 8.5 \times 10^4$ ppm by wt; $\Delta H = 7.6$ kcal/mole; $Q = 8.3$ kcal/mole; and $Q^* = 6.0$ kcal/mole. The first four quantities are those found from measurements of the terminal solid solubility and diffusion of hydrogen in zircaloy-2 [7]). The theoretical hydrogen distribution in the single-phase region was obtained by choosing an experimental point near the concentration discontinuity and adjusting C_0 in eq. (12) to pass through it. The point at which the concentration on this curve corresponded to terminal solid solubility was taken as the position of the discontinuity. This treatment accounted for any hydrogen picked up during the experiment.

The agreement between experiment and theory is seen to be good in both figs. 4 and 5, implying that within the range of hydrogen concentration encountered in the experiments the assumptions made in the model are valid. Since no normalization factor was employed in fitting the theoretical curve to the experimental points in the two-phase region, the good agreement, not only in the shape of the curve but also in absolute value, attests to the accuracy of the diffusivity and solubility values used in the calculation.

Markowitz [1]) has reported a thermal-diffusion experiment with hydrogen in zircaloy-2 where the colder portion of the specimen was in the alpha-hydride region. The hydrogen-distribution curve obtained by Markowitz (fig. 6) is relatively

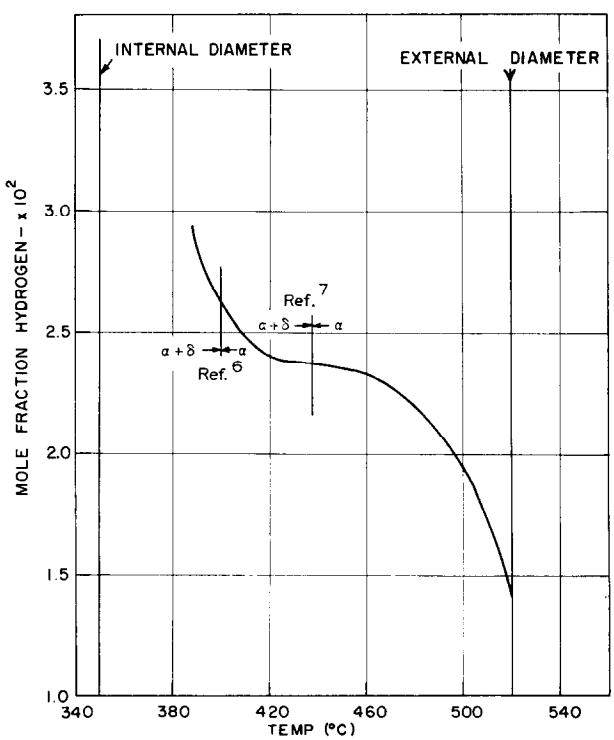

Fig. 6. Hydrogen distribution in internally cooled zircaloy-2 cylinder under a thermal gradient. (J. M. Markowitz.)

smooth with an indication of a sharp increase in hydrogen concentration near the cold surface of the specimen. However, in contrast to the results presented in figs. 4 and 5, the interface between the single- and two-phase regions, using Gulbransen's [8]) results for the terminal solubility of hydrogen in pure zirconium, falls on the smooth portion of the curve of concentration vs temperature. If the latest values for the terminal solid solubility of hydrogen in zircaloy-2 [7]) are used to establish the position of the interface, it is seen (fig. 6) to fall at the point of sharply increasing hydrogen concentration; this is in agreement with the results of the present investigation.

In section 3.3 it was predicted that in the case of a defected zircaloy-2 fuel element, where corrosion on the hot inner sheath surface can occur, the position of maximum hydriding may be fixed at a distance from the cold surface depending on the rate of hydrogen pickup. This effect is illustrated in fig. 7 which is a photomicrograph of a section near a defect in the zircaloy-2 cladding of a UO_2 fuel element which had been irradiated in a high-pressure, high-temperature loop [9]). The maximum sheath thickness was 0.070 cm with the inner and outer surface temperatures being approximately 270° and 330° C respectively. The region of heaviest hydriding is roughly 0.01 cm from the cold surface opposite the area of maximum corrosion on the hot surface. As predicted in section 3.3 this region moved toward the cold surface with increasing distance from the area of heaviest corrosion and presumably maximum rate of hydrogen pickup. It should be pointed out that the photomicrograph was taken from a polished section after cooling to room temperature. Since the cooling rate of the specimen was relatively slow (several hours to reach room temperature), a lot of the hydrogen in the single-phase region would have precipitated out. This accounts for the hydride platelets between the heavily hydrided band and the inner sheath surface.

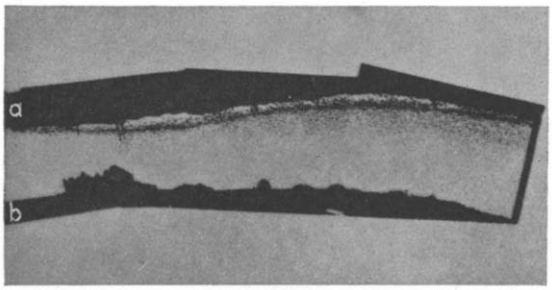

Fig. 7. Section through X-2-g sheath failure after 40 days' testing under a heat flux of 100 watt/cm². Coolant water at 965 psi and 250°–277° C. (T. J. Kisiel.)
(*a*) External cool surface. (*b*) Internal hot surface.

Acknowledgments

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