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HYDROGEN REDISTRIBUTION IN THIN PLATES OF ZIRCONIUM UNDER LARGE THERMAL GRADIENTS

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by

J. M. Markowitz

January 1958

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HYDROGEN REDISTRIBUTION IN THIN PLATES OF ZIRCONIUM UNDER LARGE THERMAL GRADIENTS

J. M. Markowitz

Introduction

It has been reported¹ that PWR Core 1-type Zircaloy clad rods have failed in in-pile tests as a result of redistribution of dissolved hydrogen to the outside of the cladding and the consequent formation of a solid hydride rim. This effect has been attributed to the thermal diffusion of hydrogen.* The probability of forming such solid hydride surface layers is enhanced by a high initial hydrogen content of the cladding.

The purposes of this study have been to:

- 1) estimate the hydrogen concentration gradients to be expected in thin (0.070 in.) Zircaloy-2 plates containing dissolved hydrogen when the plates are subject to thermal gradients up to 4000°F/in. and calculate the maximum allowable initial hydrogen concentrations if no zirconium hydride precipitation is to occur in a Zircaloy plate subject to such thermal gradients;
- 2) estimate the thickness of the hydride film formed if the specified maximum is exceeded by any given amount;
- 3) calculate the hydride-free lifetime of a Zircaloy plate with a 630°F metal surface temperature and a 750°F heat source, assuming that a given percentage of the corrosion product hydrogen dissolves in the zirconium; and
- 4) calculate pumping times and conditions required to reduce the hydrogen concentration of zirconium plate subassemblies to various concentrations.

Summary

By using experimental data*, the quantities determining the extent of dissolved hydrogen redistribution under a thermal gradient in Zircaloy were calculated. The basic quantity determining this redistribution, the heat of transport, amounts to 4.2 to 7.1 kcal/mole, depending on the

*From further work by the author, now in progress.

particular data used. With a heat of transport value, the concentration gradient resulting from the exposure of 0.070 in. thick Zircaloy plates having initial hydrogen contents of 25 to 200 ppm to center-to-surface temperature gradients of 120°, 220°, and 320°F were calculated. At a fixed surface temperature of 630°F, precipitates of zirconium-hydride would form at the surface of plates with average hydrogen contents of 50-60 ppm and at approximately 100 ppm hydrogen the thickness of this layer would increase to about 0.2 mils.

Because hydrogen is picked up by Zircaloy both during operation in high temperature water as well as during pre-operation corrosion testing, estimates were also made of the life prior to the formation of a solid hydride layer of both 70-mil platelets exposed to water on each side and of 25-mil claddings exposed to water on only one side. It was found that to prevent formation of a hydride rim at exposures of 1 year or less, initial hydrogen contents should be limited to 20-40 ppm, depending on the thermal gradient to which the material is to be exposed. If it is assumed that a hydride rim of 0.2-mil thickness could be tolerated on a 70-mil plate under a thermal gradient of 630°-750°F, the initial hydrogen content could be permitted to rise to 78 ppm without forming rims exceeding this thickness in 1 year or less; on the other hand, at a 30-ppm initial hydrogen content, the time required to form rims of such thickness during operation is 4 years.

By using available data for the diffusion rate of hydrogen in alpha-zirconium, it has been determined that a steady-state distribution of hydrogen will be achieved in times that are insignificant compared with anticipated core lives but large compared with the time for transient or accident phenomena. Thus, no benefit can be derived by increasing allowable hydrogen contents from consideration of the time required to obtain the redistribution. However, the more severe gradients encountered during such conditions as power excursions are of too short duration to affect the distribution achieved during steady-state conditions.

Because utilizing fuel elements containing as low an initial hydrogen content as possible is desirable, the feasibility of reducing the hydrogen content by a high temperature vacuum treatment in a typical configuration such as that of the PWR Seed 1 cluster was investigated. It was found

that the practicable extent to which the hydrogen content could be reduced by pumping on such a cluster is limited neither by system pumping speed nor diffusion rate of hydrogen in Zircaloy but by the physical configuration of the long thin channels. Control of initial hydrogen content thus appears to be best accomplished in the raw material and processing stages rather than in the final configuration.

1. Theory

The theoretical basis of the thermal diffusion effect is well known and has been widely discussed in the literature.^{2,3} The central idea of the theory is that under certain conditions matter transport can occur in a thermal gradient in a direction and to an extent determined by certain physical and thermodynamic properties of the substance involved. In a binary solution with only one component migrating, a steady state is reached when the concentration gradient flux which builds up as a result of thermal diffusion becomes equal to the thermal gradient diffusion flux. Under these circumstances the net flow vanishes and

$$J_1 = - \frac{D_1 N_1}{RT} \left[RT \frac{d \ln N_1}{dx} + \frac{Q^*}{T} \frac{dT}{dx} \right] = 0 \quad (1)$$

where J_1 is the net flux of the migrating component,

N_1 is its mole fraction,

D_1 is the isothermal diffusion coefficient,

R is the gas constant,

T is the absolute temperature and,

x is the coordinate through the diffusion region.*

The heat of transport, Q^* , occupies a central place in the theory. Equation (1) can be written

$$d \ln N_1 = - \frac{Q^*}{RT^2} dT \quad (2)$$

*Derivations of Eq. (1) may be found in references (2) and (3).

which becomes upon integration

$$\ln N_1 = \frac{Q^*}{RT} + C_1 \quad (3)$$

or

$$N_1 = C_2 e^{Q^*/RT} \quad (4)$$

If integration is performed between definite limits, $(N_1)_{T_1}$ and $(N_1)_{T_2}$, the mole fractions of component 1 corresponding respectively to temperatures T_1 and T_2 , the result is

$$\ln \left[\frac{(N_1)_{T_1}}{(N_1)_{T_2}} \right] = \frac{Q^*}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{Q^*}{R} \frac{(T_2 - T_1)}{T_1 T_2} \quad (3b)$$

or

$$(N_1)_{T_1} = (N_1)_{T_2} \exp \left[\frac{Q^*(T_2 - T_1)}{RT_1 T_2} \right] \quad (4b)$$

Equations (3b) and (4b) illustrate the effect of the thermal gradient somewhat better than the analogous equations (3) and (4). From Eq. (4) it is evident that the sign of Q^* determines the direction of the thermal transfer of component 1: a positive sign indicates a decrease of N_1 with increasing temperature, i.e., flow to the cold side; a negative sign causes the opposite effect. The magnitude of Q^* and the temperature difference determine the extent of the redistribution. This may be most easily seen from Eq. (4b), in which the temperature difference, $T_2 - T_1$, is to be taken as positive. Note that in the steady state the amount of redistribution depends not only on the magnitude of the gradient but is also dependent on the magnitudes of the end temperatures between which the integration is performed. Therefore, the "shape" of the temperature gradient, whether it be linear, quadratic, etc., affects the shape of the concentration gradient but not the end-point concentrations of the redistribution.

2. Calculations

a. The Thermal Gradient

A thermal gradient applicable to the present problem was first calculated. The steady-state equation for the region ($0 \leq x \leq a$),

$$\frac{d^2 T}{dx^2} + \phi = 0 \quad (5)$$

where ϕ is a source function was solved, subject to the conditions

$$T_a = T_o = \text{constant} \quad (6)$$

$$T_{a/2} = \text{constant} \quad (7)$$

The solution is

$$T = -\frac{4\Delta T}{a} \left(-\frac{x^2}{a} + x \right) + T_o \quad (8)$$

where ΔT is the temperature difference, $T_{a/2} - T_a$ or $T_{a/2} - T_o$. The temperature gradient is

$$\frac{dT}{dx} = \frac{4\Delta T}{a} \left(1 - \frac{2x}{a} \right) \quad (9)$$

Note that the temperatures calculated from Eq. (8) do not have any basis in assumptions or data on the actual thermal conductivity or rate of heat generation in the fuel plates being considered. The temperature gradient is based solely on reasonable estimates of steady-state center and surface operating temperatures.

b. Thermal Diffusion

Equation (4) was used to calculate the concentration gradient. For the case in which the specimen has at all points an initial concentration less than the terminal solubility of hydrogen in zirconium,^{4,5} the value of the constant C_2 was determined from the boundary condition that the hydrogen is conserved, i.e., for unit area of metal

$$\frac{1}{a} \int_0^a N_1 dx = N_o \quad (10)$$

where N_o is the original constant concentration of hydrogen. On introducing Eq. (4), Eq. (10) becomes

$$C_2 = \frac{aN_o}{\int_0^a \frac{e^{Q^*/RT}}{dx}} \quad (11)$$

The integration required in Eq. (11) was performed numerically with values of T calculated from Eq. (8). Equation (4) was used with the calculated value of C_2 to obtain the concentration gradient. In Fig. 1, curves 1, 2, and 3 represent the results of this calculation for specimens having an initial uniform concentration of 25 ppm and subjected to the temperature gradients indicated on the figure.

For the case of specimens whose initial concentration locates them, when placed in the desired thermal gradient, so that the concentration crosses or lies to the hydride side of the terminal solubility line for hydrogen in zirconium,^{4,5} the process of thermal diffusion is more complex, leading to precipitation of hydride at the cold end of the specimen and the creation of a concentration gradient in the solid solution which is left. The process by which this occurs is presented in Fig. 2, in which the temperature-composition relationships shown by the graphs on the left correspond to the pictorial representations of the Zircaloy sections on the right. The shaded portion represents the presence of hydride, the relative amount being indicated by the heaviness of shading. The heavy lines on the graphs represent the point concentrations in the solid solution matrix; the vertical line, curve 1, and the curved line, curve 2, are, respectively, the initial uniform concentration and the terminal solubility line, i.e., the boundary of the single-phase region on the phase diagram. Figures 2a, b, c and d are consecutive stages in the hydrogen redistribution process.

Initially, the situation in Fig. 2a prevails; the uniform concentration of hydrogen is undisturbed, and the hydride is in equilibrium with solid solution at every point in the temperature gradient. When thermal diffusion begins in the solid solution, a gradient of concentration is established as shown in Fig. 2b. The hydrogen moving away from the hot side then would tend to accumulate as hydride at the point where curves 1 and 2 cross, except that the amount of hydride at this and all lower temperatures is fixed by the terminal solubility line, curve 2. Therefore, the tendency for hydrogen to accumulate is

counteracted by flow of hydrogen toward regions of lower matrix concentration, i.e., downward along curve 2. Ultimately, pure hydride must precipitate at the point where the matrix hydrogen concentration is least, at the cold end of the specimen.

As the process proceeds to a stage beyond that represented by Fig. 2b, hydride initially present at the higher temperatures begins to dissociate and go into solution to counteract the depletion of hydrogen caused by thermal diffusion in the matrix. This dissolution is progressive, the hydrogen being reprecipitated at the cold end until, finally, the steady state depicted in Fig. 2d is reached (Fig. 2c shows an intermediate stage).

At the end of the process the solid solution at the cold end of the specimen is in equilibrium with hydride at the same temperature; the boundary condition for this case (obviously hydrogen is not conserved in the solid solution) is that the matrix concentration at the cold end of the gradient must be equal to the terminal solubility at that temperature. Thus, by using Eq. (4)

$$N_{eq.} = C_2 e^{Q^*/RT} \quad (12)$$

Equation (12) is used to evaluate C_2 , and Eq. (4) is then used to calculate the diffusion gradient. In the actual calculations, the value of $N_{eq.}$, the terminal solubility, was taken both from the data of Gulbransen and Andrew⁴ and from those of Albrecht, Schwartz* and Mallett.⁵ The values differ by about 20 ppm. The use of the lower value⁴ results in a smaller limit for the amount of hydrogen that can be tolerated without hydride precipitation; this limit will be called the critical concentration. Terminal solubility data from both references are plotted in Fig. 1.

To determine the amount of hydride precipitate produced after a thermal gradient anneal of a specimen containing a given initial hydrogen concentration, the total number of moles of hydrogen contained in the final solid solution, n^f , was calculated numerically by the formula

$$n^f \cong \frac{\rho_{Zr}}{2M_{Zr}} \int_0^a N_1 dx \quad (13)$$

*Reference 5 includes the data of investigations by Schwartz, as indicated on the curves.

where ρ_{Zr} and M_{Zr} are, respectively, the density and molecular weight of zirconium, and 2 is the molecular weight of hydrogen. The total amount of hydrogen present before anneal is

$$n^i = \frac{\rho_{\text{Zr}}}{2 M_{\text{Zr}}} a N_0 \quad (14)$$

so that the amount of hydrogen in the precipitated hydride is

$$n^{\text{ppt}} = n^i - n^f \quad (15)$$

On assuming the formula Zr_2H_3 for the precipitate, the number of moles and, therefore, the weight of the precipitate were calculated. The thickness is (since all calculations have been based on unit area) the calculated weight divided by the density, for which the value 5.61 g/cm^3 was used.⁶

In the foregoing calculations two values were used for Q^* . The value of 4.2 kcal/mole was determined experimentally* from analysis after thermal gradient anneal of a Zircaloy-2 specimen with a concentration of hydrogen that placed the specimen entirely in the single-phase region of the phase diagram. The second value, 7.1 kcal/mole , was calculated by Shewmon⁷ from data* on a specimen whose concentration placed it partly in the single-phase region. Both sets of data are plotted in Fig. 3. In the second case, thermal diffusion was only partly completed and only a portion of the data could be used for the determination of Q^* . Accordingly, the first value quoted, 4.2 kcal/mole , is considered more reliable, although calculations were performed based on both values. The results are compared in curves 4 and 5 of Fig. 1; the former curve corresponds to the higher value of Q^* , 7.1 kcal/mole . The higher value leads to a greater redistribution of hydrogen and therefore sets a smaller limit on the initial amount of hydrogen which can be tolerated without hydride precipitation.

A lower limit for the time required to sweep the hydrogen out of a specimen of zirconium and form hydride at the cold end can be estimated by a procedure devised by Shewmon.⁷ The time is taken as

*From further work by the author, now in progress.

$$t = \frac{(N_1^h - N_1^c)}{J_1} X_s \quad (16)$$

where N_1^h and N_1^c are average hydrogen concentrations to the hotter and colder sides of a coordinate, taken here as the midline of the specimen. The term J_1 is the flux of hydrogen which may be calculated from Eq. (1), ($J_1 \neq 0$) as follows:

In Eq. (1) if local thermodynamic equilibrium is obtained at each point of the gradient, the first term in the brackets may be given by the equilibrium equation:⁸

$$RT \frac{d \ln N_1}{dx_1} = \frac{\Delta \bar{H}_1}{T} \frac{dT}{dx} \quad (17)$$

where $\Delta \bar{H}_1$ is the partial molar heat of solution of hydrogen in alpha zirconium. Upon substitution of Eq. (17) into Eq. (1),

$$J_1 = \frac{D_1 N_1}{RT^2} (\Delta \bar{H}_1 + Q^*) \frac{dT}{dx} \quad (18)$$

The value of $\Delta \bar{H}_1$ has been determined to be 8.6 kcal/mole by Gulbransen and Andrew.⁴ Albrecht, Schwartz and Mallett⁵ give D_1 as a function of temperature. Upon carrying the calculation through for a typical condition considered in the previous calculations, the time is computed to be of the order of 4 days. This means that short time or transient reactor conditions, under which sudden increases in thermal gradient occur, would not contribute substantially to the movement of hydrogen and also that the time for achievement of steady state is too small, compared with a reasonable core lifetime, for any substantial benefit to be derived in increasing allowable hydrogen contents on the basis of the time required for redistribution.

c. Hydrogen Pickup Due to Corrosion

To obtain a figure for the contribution to hydrogen concentration in a Zircaloy plate under operating conditions due to the corrosion reaction

the corrosion weight change shown in curve 1 of Fig. 4 was assumed. The

data plotted in this curve were interpolated from the most recent experimental results available* for the weight change per unit area as a function of time of exposure; curve 1 applies to 630°F water. Shown also in Fig. 4 are two curves representing the increase of hydrogen concentration in Zircaloy specimens as a result of corrosion, assuming that 25% of the hydrogen produced by the corrosion reaction enters the zirconium lattice: curve 2 is for a 25-mil cylindrical clad, and curve 3 is for a 70-mil plate. These curves were derived by the use of the following equation, which gives the increase in hydrogen content in the Zircaloy when one surface is exposed to water at the specified temperature:

$$c_H = 0.0187 W/a \quad (19)$$

where

W is the weight gain in mg/dm^2 , which is read off curve 1 of Fig. 4;

a is the thickness of the metal in mils; and

c_H is the hydrogen concentration in ppm.

The calculated concentration increase from Eq. (19) must be multiplied by 2 for a plate since both surfaces are attacked. The amount of hydrogen produced the corrosion which actually enters the lattice appears to vary with exposure time**; however, 25% entry is a reasonable overall estimate.

The effect of hydrogen introduction through the corrosion reaction is, of course, to reduce the amount of hydrogen which can be tolerated initially if hydride precipitation is to be prevented or kept below some specified level. Figure 5 shows the results of calculations made to determine the magnitude of this effect in several cases: a cylindrical cladding under a 120°F gradient with no hydride tolerated; a plate under a 320°F gradient with no hydride tolerated; a plate under a 120°F gradient with no hydride tolerated; and a plate under a 120°F gradient with 0.2-mil hydride rim tolerated. It was assumed that the specimens were exposed to 750°F steam for 3 days in corrosion testing before being operated in water at a 630°F surface temperature. The amount of hydrogen introduced by the former treatment amounts to 13.1 ppm for the cylindrical

*R. Lennon, Bettis Atomic Power Division.

**K. E. Goldman, Bettis Atomic Power Division.

clad and 9.5 ppm for the plate.* The toleration limits for the cases mentioned arise from the thermal diffusion effect discussed earlier; the limits are given by the curves of Figs. 6 and 7 (to be discussed later) that present, respectively, the critical hydrogen concentration at which precipitation begins for various initial conditions and the thickness of hydride rim to be expected when the hydrogen concentration initially exceeds the critical concentration. The difference between the critical concentration and the amount of hydrogen initially present is the concentration that can be tolerated from corrosion. The 3-day corrosion test hydrogen accumulation was subtracted from this difference; what remains is the amount of hydrogen pickup that can be tolerated under operating conditions. The lifetime corresponding to this amount of pickup was read off on Fig. 4, curves 2 and 3, and plotted against the initial concentration on Fig. 5; the four cases mentioned above are plotted there as curves 1, 2, 3, and 4, respectively.

d. Removal of Hydrogen by Pumping

The calculation of time of pumping required for specified reduction of the hydrogen content of Zircaloy plates prior to operation is based on the work of E. W. Johnson,⁹ who considered the analogous problem of removing hydrogen from titanium. Johnson considers that degassing rates are determined by one of three independent processes: (1) removal rate determined by pumping speed; (2) removal rate determined by solid diffusion; (3) removal rate determined by gaseous diffusion. He presents methods of calculating the time necessary to pump gas out of a metal from a given initial concentration to any final concentration for any of these three cases. Little attention need be given to the first case, since calculations using pumping time curves for several pumping arrangements presented by Johnson show this process to be very fast for amounts of dissolved hydrogen up to several hundred ppm.

If the second process, lattice diffusion of hydrogen in zirconium, is the limiting process, the removal rate depends on the diffusion coefficient of hydrogen in zirconium and is also quite sensitive to

*R. Lennon.

specimen geometry. The degassing time is given, for plate geometry, by

$$t = \frac{W^2}{4.29 D} \log \left[0.81 \left(\frac{C_1 - K\sqrt{P}}{\bar{C} - K\sqrt{P}} \right) \right] \quad (20)$$

where

W is the plate thickness, in.

D is the diffusion coefficient for hydrogen in zirconium, in.²/hr

C₁ is the initial concentration

$\bar{C}$ is the average final concentration, ppm

p is the ultimate pressure produced by the pumps, microns and

K is Sievert's constant, as used in Sievert's Law ($C_H = K_p^{1/2}$) (21)

which relates the concentration of hydrogen in zirconium to the partial pressure of hydrogen gas in equilibrium. For the units of Eq. (20), K must be in ppm-microns^{-1/2}. Calculations based on Eq. (20) and values of D and K from reference (5) give pumping times of the order of a fraction of an hour for a 70-mil Zircaloy plate weighing 2.5 lb that is being pumped on in an enclosure at 750°C. Thus, in thin components solid state diffusion does not generally limit hydrogen removal.

The third process cited involves the removal of dissolved gas from closely spaced sheets or plates of metal. The gas must first reach the metal surface and then pass down the channel between the sheets toward the pumps. The latter process is controlled by gaseous diffusion, with one important qualification: the pressure at any point in the channel is fixed through Sievert's Law, Eq. (21) by the concentration of hydrogen in the nearby metal. Thus, although flow in the channel proceeds by a diffusion mechanism, the pressure gradient in the channel is governed not by diffusion but by the point-to-point concentration along the metal sheet surface. If initially uniform, this point-to-point concentration soon assumes a gradient because of the greater proximity of the sheet edges to the pumps. After a certain induction period, however, the pressure gradient in the channels can change only very slowly, both because gaseous diffusion through the channels is slow and gas pressure at every point remains close to equilibrium with the dissolved hydrogen in the metal.

In treating this situation, Johnson⁹ combined the kinetic theory equation for the rate of molecular flow in narrow channels with equations for the hydrogen gas-dissolved hydrogen interaction (based on Sievert's Law) to derive an effective diffusion coefficient, D , given in in.²/hr by

$$D = 0.49 \times 10^6 \frac{b^2 C_a}{K^2 W \delta} \sqrt{\frac{2}{T}} \quad (22)$$

where

b is the sheet spacing, in.

K is Sievert's constant,

W is the sheet thickness, in.

C_a is the final concentration in the sheet

δ is the metal density in lb/liter and

T is the absolute temperature.

This value of D applies to gaseous diffusion through the channels and can be used in an equation of the same form as equation (21) except that L , the sheet width, must be substituted for W in the latter. Thus,

$$t = 4.75 \times 10^{-6} \frac{L^2 K^2 W \sqrt{T}}{b^2 C_a} \log \left[0.81 \left(\frac{C_1 - K \sqrt{P}}{C_a - K \sqrt{P}} \right) \right] \quad (23)$$

Note in Eq. (23) that the pumping time varies inversely as the square of the sheet spacing and directly as the square of the sheet width. Thus, for small spacings and long sheets the pumping time becomes extremely long. For PWR seed plates, $L = 72$ in., $W = 0.066$ in. and $b = 0.066$ in. Upon introducing these quantities,

$$t = 0.373 \frac{K^2 W \sqrt{T}}{C_a} \log \left[0.81 \left(\frac{C_1 - K \sqrt{P}}{C_a - K \sqrt{P}} \right) \right] \quad (24)$$

Equation (24) was used in the calculation of the pumping time required to reduce the hydrogen concentration of entire subassemblies. Results appear in Fig. 8, and are discussed in Section 3d.

3. Results and Discussion

a. Expected Hydrogen Concentration Gradients and Critical Concentrations

Examples of concentration gradients to be expected in Zircaloy plates of initially uniform concentration as a result of the thermal diffusion process are presented in Fig. 1. This diagram, in which temperature is plotted against hydrogen concentration, shows the region of concentration and temperature in which hydrogen can exist in alpha zirconium as a solid solution and the region in which two phases, alpha solid solution and zirconium hydride, must form. These regions are separated by the terminal solubility line, which thus represents the maximum concentration for a given temperature, at which hydrogen can exist in zirconium without hydride precipitation. In Fig. 1, two terminal solubility curves are drawn: curve 6 represents the data of Gulbransen and Andrew⁴ and curve 7, those of Albrecht, Schwartz, and Mallett.⁵ There is little reason to prefer one set of data over the other except that the data of Gulbransen and Andrew, lying some 20 ppm lower than those of Albrecht, Schwartz, and Mallett, result in the establishment of smaller, and therefore more conservative, concentration limits for hydrogen.

Curves 1, 2, and 3 of Fig. 1 show the concentration gradients resulting when a 70-mil plate with an initial hydrogen content of 25 ppm and a surface temperature of 630°F is exposed to temperature gradients of 120°, 220°, and 320°F, respectively. Depending on the shape of the temperature gradient, the ordinate corresponds to various positions in the plate thickness. No hydride precipitation occurs, but the low temperature end of the concentration gradient lies closer to the terminal solubility curve as the temperature gradient increases. On cooling such a plate to room temperature, the concentration gradient will be evidenced by a more profuse precipitation of hydride of the cold end of the specimen. Curve 5 represents the concentration gradient resulting when a plate with an initial hydrogen concentration of 62 ppm and with a surface temperature of 630°F is exposed to a temperature gradient of 220°F. This may also be interpreted as the steady-state concentration gradient in the solid solution portion of a specimen with an initial hydrogen concentration

greater than 62 ppm and subjected to the same temperature gradient, i.e., a specimen that has passed through the process of sweeping out of hydride described earlier and shown in Fig. 2. Since hydride precipitation occurs in this process, it is evident that 62 ppm is the maximum hydrogen concentration that can be tolerated under the stated conditions without the occurrence of hydride precipitation. Curves 4 and 5 show the effect on the concentration gradient of the magnitude of Q^* : values of 7.1 and 4.2 kcal/mole, respectively. The critical concentration corresponding to Q^* of 7.1 kcal/mole is 48 ppm; in contrast, the value 62 ppm (cited above for the lower value of Q^*) shows that the higher the value of Q^* , the lower the critical hydrogen concentration.

The foregoing results are summarized in Fig. 6, which plots the critical hydrogen concentration at steady state vs. the high-side temperature, in all cases for a surface temperature of 630°F. Contrasting curves 1 and 2 shows the effect of the choice between the terminal solubility data from the two sources cited; the critical concentration is at every high-side temperature some 20 ppm greater, if the data of Albrecht, Schwartz, and Mallett⁵ are accepted over those of Gulbransen and Andrew.⁴ Curves 2 and 3 compare the effect of the magnitude of Q^* ; acceptance of the 4.2 kcal/mole figure results in critical concentrations some 13 ppm higher than those resulting from the choice of 7.1 kcal/mole. As stated previously, the value of 4.1 kcal/mole seems better founded. Therefore, on the whole, the choice of curve 2 of Fig. 6 as a basis for core design specifications seems most conservative and reliable.

b. Hydride Film Thicknesses

It has been shown that if the critical hydrogen concentration for a Zircaloy plate in a given temperature gradient at a fixed surface temperature is exceeded, a zirconium hydride layer will form on the cold side. The thicknesses of the hydride rims formed for various initial conditions were calculated by the method described in Section 2 and the results plotted in Fig. 7, which presents a family of curves of hydride layer thickness vs. initial concentration. Three of the curves correspond to the choice of any of three temperature gradients. The remaining curves show the effect on hydride thickness of the use of a Q^* value of 7.1 rather than 4.2 kcal/mole, and the effect of the use of the terminal solubility

data of Albrecht, Schwartz, and Mallett⁵ rather than that of Gulbransen and Andrew.⁴ It is seen that for a given initial concentration, more hydride is formed in larger gradients; also, the larger the value of Q^* , the thicker the hydride rim. The use of the higher terminal solubility data⁵ leads to the expectation of less hydride formation than the use of the alternative data.⁴ From another point of view, if a given amount of hydride can be tolerated, the acceptable initial hydrogen concentration rises as the temperature gradient decreases, as the value of Q^* becomes smaller, and as the terminal solubility is higher.

c. The Hydride-free Lifetime in Operation

Figure 5 shows the operating life of 25-mil cylindrical cladding and 70-mil fuel plates exposed to high temperature water vs. the initial hydrogen concentration. As explained in Section 2, the operating lifetime is based on the tolerable amount of hydrogen pickup both from pre-operational corrosion testing and from the corrosion reaction during operation. Curve 1 shows that in a 120°F gradient, a cylindrical clad must have an initial hydrogen concentration of 30 ppm or less if the hydride-free lifetime is to be 1 year or more. For a plate under the same conditions curve 3 shows that almost 40 ppm can be tolerated initially. However, if the operating temperature gradient is increased to 320°F, the amount of hydrogen that can be tolerated initially is cut almost to 20 ppm if the same service life is expected (curve 2). If some hydride formation is permitted, the permissible initial hydrogen content can be increased greatly as shown by curve 4, from which it is seen that almost 80 ppm of hydrogen can be tolerated initially in a plate under an operating gradient of 120°F if a 0.2-mil of hydride rim is acceptable.

d. Pumping Conditions for Hydrogen Removal from Zircaloy Plates

Calculations discussed in Section 2 showed that the pumping time for removal of hydrogen from PWR Seed 1-type plates is comparatively short if individual widely spaced plates are pumped on at a fairly high but easily realizable temperature, 750°C. This is the case whether the slow process in reducing the hydrogen concentration is the pumping speed limitation of the experiment or the rate of diffusion of hydrogen through

the zirconium lattice. Thus, removing hydrogen from Zircaloy is a relatively easy matter for unassembled plates.

It would be economically desirable, however, to reduce the hydrogen content at the latest point possible in manufacture, for example, removal from a welded subassembly. This situation corresponds to a very closely spaced array of plates, the plate-to-plate clearance being of the same order as the plate thickness, 66 mils. For such an assembly, the rate is very much slower, as shown in Section 2, than for the same number of widely spaced plates. The fact that the plates are not exposed to the pumps except at their ends makes effective width of the pumping channels the full 72-in. length of the subassembly. This factor also contributes to the increase in pumping time, which is proportional to the square of the channel width.

Pumping time calculations for the reduction of hydrogen content in subassemblies under various pumping conditions by the use of Eq. (24) lead to the results shown in Fig. 8, where the required pumping time is plotted against the desired final concentration; uniform initial concentration of 100 ppm in a PWR Seed 1-type subassembly was assumed in all cases. Curves 2 and 3 compare the effect of pumping system efficiency on the pumping time at a furnace temperature of 750°C. For curve 2, the vacuum at the pump throat is assumed to be 0.01 microns, which represents excellent performance for a reasonably sized commercial pumping station with an oil diffusion pump. For curve 3, the vacuum at the pump throat is assumed to be 1 micron, which represents the ideal performance to be expected of a pumping station equipped only with mechanical pumps. Even for the superior pumping system, 50 hr would be required to reduce the average hydrogen content to 30 ppm. At points near the middle of the plates the local concentration might be much higher than this. Curves 3, 4, and 5 and curves 1 and 2 may be compared to judge the effect of furnace temperature on pumping speed; these curves show that the effectiveness of an increase in furnace temperature diminishes as the temperature is raised and that increase of temperature is more effective in reducing pumping time when the ultimate vacuum is lower. The best figure possible from these calculations is a 24-hr pumping time to reduce the hydrogen concentration to 30 ppm at 850°C. No improvement

is possible from further temperature increase because at higher temperatures the Zircaloy transforms to the β -phase; Sievert's constant, to the square of which the pumping time is proportional, is approximately doubled in β -zirconium at 850°C.

4. Conclusions

The general conclusion from this report is that the phenomenon of hydride precipitation by means of thermal gradient diffusion of dissolved hydrogen in Zircaloy fuel plates and cladding places much more severe restrictions on the allowable pre-operation hydrogen content of such elements than has been hitherto suspected. The specific restrictions which must be employed for design purposes are governed not only by the anticipated operating conditions of the element and the desired operational life-time but by design judgment, in each individual case, of the amount of hydriding that can be tolerated. No such judgment is appropriate or warranted in this report. However, once such a judgment is made, the allowable pre-operation hydrogen content can be established from the material included here.

The specific effects of operating conditions on the hydrogen content of plates and cladding are presented in detail in the body of the report. The following table summarizes the principal trends and magnitudes encountered.

	Temp. Gradient ^c (°F)			Q* ^d (kcal/mole)		Solubility Limit ^e Reference	
	120	220	320	4.2	7.1	4	5
Critical Hydrogen Conc., ppm	70	62	53	70	56	70	91
Hydride Thick- ness, mils ^a	0.14	0.19	0.23	0.14	0.21	0.14	0.04
Hydride-free Life, years ^b	1.53	1.02	0.55	1.53	0.62	1.53	2.8
^a Initial concentration, 100 ppm							
^b Initial concentration, 30 ppm							
^c Q*, 4.2 kcal/mole; Terminal solubility, reference 4							
^d Gradient, 120°F; Terminal solubility, reference 4							
^e Gradient, 120°F; Q*, 4.2 kcal/mole							

REFERENCES

1. J. D. Eichenberg, et al., "Effects of Irradiation on Bulk UO_2 ," WAPD-183, October 1957.
2. S. R. DeGroot, Thermodynamics of Irreversible Processes, Interscience Publishers Inc., New York, 1952.
3. K. G. Denbigh, The Thermodynamics of the Steady State, Methuen Monograph, London, 1951.
4. E. A. Gulbransen and K. F. Andrew, Trans. Am. Inst. Mining Met. Engrs., 203, 136 (1955); J. Electrochem. Soc., 101, 560 (1954).
5. M. W. Mallett and W. M. Albrecht, J. Electrochem. Soc., 104, 142 (1957).
6. M. W. Mallett and V. M. Shipline, "Hydrides," Chapter 1.10, p. 167 (Unclassified), The Reactor Handbook, Vol. 3, Materials, Technical Information Service, USAEC, 1953.
7. P. G. Shewmon, Westinghouse Research Laboratories Scientific Paper 94701-2-P7, 1957.
8. L. Darken and R. Gurry, Physical Chemistry of Metals, McGraw-Hill Book Co., New York, 1953.
9. E. W. Johnson, Westinghouse Research Laboratories Research Report 60-8-10-04-R1, 1955.

Fig. 2 Thermal Diffusion in the Two Phase Region

FIGURE 3

Fig. 8 Removal of Hydrogen from PWR Type Seed Clusters (Initial Conc., 100 pp)