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IN
DELTA-PHASE ZIRCONIUM HYDRIDE
(Title Unclassified)

AEC Research and Development Report

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IN
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(Title Unclassified)

By

S.D. HARKNESS

and

W.A. YOUNG

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ABSTRACT

Diffusion coefficients of hydrogen in δ -phase SNAP fuel were determined from experimental hydrogen sorption curves for H/Zr atom ratios of 1.50 to 1.80 and for the temperature range of 650 to 900°C. The values fit the expression:

$$D = \left(1.3^{+5.8}_{-1.1}\right) \times 10^{-2} \exp - \left(\frac{12690 \pm 3444}{RT}\right)$$

The results are compared with those obtained by other authors for diffusion of hydrogen in zirconium and titanium hydrides. An analysis of the experimental errors indicates an uncertainty of $\pm 25\%$. No concentration dependence was observed for the diffusion coefficients. Tests using pure zirconium hydride and unmodified fuel indicate that neither carbon nor uranium have any effect on the diffusion of hydrogen in δ -phase fuel.

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I. INTRODUCTION

The evolution of hydrogen from SNAP fuel (hydrided alloy of 90% Zr, 10% U, with 0.15% C) will have three primary effects on the fate of the fuel upon its reentry into the atmosphere. First, the evolution process is endothermic and, hence, will tend to retard heating of the fuel. Second, evolving hydrogen will tend to disrupt surface films formed by oxidation of the fuel and thus alter heat transfer characteristics of the films. Third, upon escaping to the atmosphere, evolved hydrogen may react with atmospheric oxygen and thus tend to increase heating of the fuel.

The importance of these effects relative to other processes which occur during reentry will be determined, in part, by the rate of evolution of hydrogen which, in turn, is dependent upon the rate of diffusion of hydrogen within the fuel. Thus, a knowledge of the diffusion coefficient as a function of temperature and composition is required for an understanding of the processes which occur upon reentry of the fuel.

The work described in this report was undertaken as a portion of the overall Aerospace Safety Program at Atomics International.

II. EXPERIMENT

It can be shown that the diffusion coefficient of a gas in a solid can be determined from changes in the weight of the gas contained within the solid during isothermal sorption of the gas. The least complex relationship between this weight and the diffusion coefficient is that obtained for the case of spherical solids. Subject to several conditions (see Section III), this relationship is

$$\frac{W_{\infty} - W_t}{W_{\infty} - W_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - \left(\frac{n^2 \pi^2 D t}{A^2} \right),$$

where

W_{∞} = weight of gas in the solid at equilibrium

W_t = weight of gas at time, t

W_0 = initial weight of gas

D = diffusion coefficient

t = time

A = radius of the sphere.

In this work, the diffusion coefficient of hydrogen is determined from the weight of hydrogen contained within the samples during hydriding or dehydriding.

A. MATERIALS

Ultrapure hydrogen was used without further purification. The manufacturer's specifications indicate a maximum of 10 ppm for the total impurity content.

Spherical samples (1.000 ± 0.005 -in. diameter) were machined from reactor grade, 0.15% carbon-modified, zirconium-10 wt % uranium alloy which had been arc-melted three times and extruded into rods (1.25-in. diameter). A typical analysis of these rods follows:

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Major Constituents

Element	wt %
U	9.95
C	0.14

Trace Elements

Element	PPM
Ag	-
Al	60
B	<0.5
Ba	<5
Be	<0.5
Bi	<2
Ca	<25
Cd	5
Co	<5
Cr	35
Cu	300
Fe	325
Hf	<200
Li	<1
Mg	<5
Mn	<10
Mo	<50
N	30
Na	<50
O	1145
Pb	<5
Si	75
Ti	<25
V	<10
W	18
Zn	<20

inserted through the bottom of the Vycor retort (see Figure 1). A Leeds and Northrup Speedo-max recorder was used to obtain a continuous record of the sample temperatures, fluctuations of 8°C were typical.

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Figure 1. Schematic Diagram of Thermocouple Placement

B. APPARATUS

The weight of each sample was obtained as a function of time by using an Ainsworth Semi-Micro Automatic Recording Balance, Type A-K, which has a sensitivity of 0.5 mg and is capable of recording a maximum weight change of 3.9 gm.

Samples were suspended within a molybdenum susceptor which was inductively heated using a 2.5-kva, Lepel high-frequency unit. The susceptor was required to shield the samples from magnetic forces produced by the induction field and thus to permit accurate weighing.

Sample temperatures were measured ($\pm 1^\circ\text{C}$) by means of two 20-mil Geminol thermocouples

Hydrogen was maintained at constant pressure within the system by means of a bellows-sealed valve and a fine needle valve in parallel, both of which were manually operated. The bellows valve was used for rapid introduction of hydrogen, the needle valve was used for admission of small amounts of hydrogen required to maintain constant pressure. A strain-gage transducer located near the sample and a Bourdon-type pressure gauge permitted measurement of the pressure within the system to ± 1 mm.

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C. PROCEDURE

The sample was placed in a weighed cage, consisting of four pieces of platinum wire, washed in pure ethanol, and suspended from the balance on a weighed stainless-steel wire. The system was then repeatedly evacuated to 10^{-5} mm and flushed with hydrogen to remove air and ethanol vapor effectively. The sample was then heated to 850°C and maintained at this temperature for 90 min in a hydrogen atmosphere; this technique has been shown^{(1)*} to be effective in removing oxide and nitride films which form a surface barrier. Temperatures and hydrogen

pressures were then adjusted to the desired values and maintained at these values until no further changes in the weight of the sample were detectable. The pressure of hydrogen was then changed by rapid (almost instantaneous) addition or removal of hydrogen. Temperatures and pressures were monitored and manually adjusted to maintain isothermal and isobaric conditions until the hydrogen sorbed by the sample reached 90% of that which would be sorbed at equilibrium. The weight of the sample was then determined as a function of time at several points on the balance recorder tracing.

*Superscripts refer to the like-numbered References at the end of this report.

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III. THEORETICAL CONSIDERATIONS AND DETERMINATION

A. THEORETICAL CONSIDERATIONS

The rate of change of concentration of a substance diffusing through a medium at constant temperature is given by Fick's second law,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right), \dots (1)$$

where

C = concentration of the diffusing species

t = time

D_x, D_y, D_z = diffusion coefficients (may be function of C) in the x, y , and z directions.

If the diffusion coefficients are independent of concentration and if diffusion in the medium is isotropic, this law (Equation 1) becomes

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) = D \nabla^2 C, \dots (2)$$

where

D = isotropic, concentration-independent, diffusion coefficient.

For spherically symmetrical diffusion, this expression reduces to

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right), \dots (3)$$

where

$r = \sqrt{x^2 + y^2 + z^2}$ = radial distance from the center of the sphere.

Crank⁽²⁾ has shown that sorption of a gas by a spherical solid is given by

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-n^2 \pi^2 D t}{A^2} \right), \dots (4)$$

provided the following conditions are met:

- 1) Fick's second law (Equation 3) is valid.
- 2) The sphere is initially homogeneous.
- 3) The radius of the sphere is constant.
- 4) The concentration of the gas in the surface of the sphere is constant and equal to the equilibrium value (i.e., transfer of gas into or from the solid is limited only by diffusion within the solid and not by processes occurring at the surface).

In this expression,

M_t = the amount of gas sorbed at time, t

M_∞ = the amount of gas sorbed at equilibrium ($t = \infty$)

A = radius of the sphere.

Since

$$\frac{M_t}{M_\infty} = \frac{W_t - W_o}{W_\infty - W_o},$$

the fraction of gas remaining to be sorbed at time, t , will be given by

$$F_t = 1 - \frac{M_t}{M_\infty} = \frac{W_\infty - W_t}{W_\infty - W_o} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(\frac{-n^2 \pi^2 D t}{A^2} \right), \dots (5)$$

where

W_∞ = weight of gas contained within the sphere at equilibrium ($t = \infty$)

W_t = weight of gas contained within the sphere at time, t

W_o = weight of gas initially present in the sphere ($t = 0$).

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For values of t approaching or greater than $A^2/\pi^2 D$, the summation in Equation 5 converges sufficiently rapidly so that only a relatively small error is introduced by neglecting all except the first ($n = 1$) term. One may then write

$$F_t = \frac{W_\infty - W_t}{W_\infty - W_0} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D}{A^2} t\right) \quad \dots (6)$$

Thus, the value of the diffusion coefficient, D , may be determined from the slope ($\pi^2 D/A^2$) of the curve on a semilogarithmic plot of F_t versus time for values of time $\geq A^2/\pi^2 D$, provided the assumptions required for the derivation of Equation 5 are valid

Fick's second law has been in general use for many years and has been shown to be valid for diffusion of hydrogen in β -phase zirconium hydride,^(1,3) it is assumed to be valid in this work. Anisotropic diffusion in cubic crystals is extremely rare, thus, since both β - and δ -phase zirconium hydride are cubic (β is B.C.C. and δ is F.C.C.), and since the samples were polycrystalline, isotropic behavior is essentially assured. The initial homogeneity of the samples was verified by metallographic examination of the fuel rods and randomly chosen spheres. The effects of changes in the radius (less than 1%) of the samples due to sorption of hydrogen and of temperature fluctuations ($\pm 8^\circ\text{C}$) are discussed in paragraph B, the assumptions of constant temperature and constant radius are valid within these experimental errors. Gelezunas⁽¹⁾ found that in the β -phase, diffusion is independent of concentration and that the surface concentration of hydrogen is constant at the equilibrium value, these assumptions are not readily subject to experimental verification but are justified if the experimental results can be expressed in terms of Equation 5.

B. DETERMINATION OF DIFFUSION COEFFICIENTS

Values of the diffusion coefficients were first determined from the slopes, λ , of semilogarithmic plots of F_t versus time, since from Equation 6

$$\lambda = \pi^2 D/A^2 \quad \dots (7)$$

These values of the coefficients ($\sim 10^{-5} \text{ cm}^2/\text{sec}$) indicated that for Equation 6 to be valid, the time, t , should be not less than $\sim 10^4$ sec. Unfortunately, sorption occurred so rapidly that the fraction to be sorbed after this time was less than 0.1 in nearly every case

Since the error due to temperature fluctuations (see paragraph C) increases rapidly as the fraction decreases below 0.1 (approaching equilibrium), data representing small fractions are unreliable. To overcome this difficulty, the diffusion coefficients were calculated, using a computer program⁽⁴⁾ devised to determine diffusion coefficients by an iterative least-square method based on Equation 5 which is applicable for any value of time. In some instances, the data fit the theoretical curve (Equation 5) obtained using the computed value of the diffusion coefficient extremely well (see Figure 2), in others (see Figure 3), the fit was less desirable. In every case, however, a more satisfactory fit of the data was obtained with the computer-calculated value than with the value given by Equation 7.

The results obtained for the diffusion coefficients of hydrogen in β -phase fuel are given in Table 1 and are indicated in Figure 4, those obtained for diffusion in δ -phase fuel are given in Table 2 and in Figure 4. The precision values given in the tables are the root mean squares of

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Figure 2. Calculated Hydrogen Sorption Curve for δ -Zirconium Hydride at 702°C

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Figure 3. Calculated Hydrogen Sorption Curve for δ -Zirconium Hydride at 718°C

TABLE 1
HYDROGEN DIFFUSION COEFFICIENTS IN
 β -ZIRCONIUM HYDRIDE

Temperature (°C)	H/Zr	Diffusion Coefficient ($\text{cm}^2/\text{sec} \times 10^{-4}$)	Precision (%)
760	0.33	1.17	7.3
763	0.58	0.95	60.1
763	0.68	0.67	24.1
802	0.50	1.54	9.8
817	0.80	2.65	2.7
834	1.05	2.13	52.3
843	0.50	1.96	13.1
843	0.70	1.87	17.1

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Figure 4. Hydrogen Diffusion Coefficients in Zr-H System

the square of the relative error at each data point; i. e.,

$$\text{precision} = 100 \times \sqrt{\frac{1}{n} \sum_{i=1}^n \frac{(F_t - C_i)^2}{F_i^2}}, \dots (8)$$

where

F_i = observed fraction

C_i = calculated fraction

n = number of data points.

C. ERROR ANALYSIS

Temperature fluctuations of the sample are the largest source of error in the measurement of the coefficients. These fluctuations will create a variable surface concentration of hydrogen which will alter diffusion rates. Gelezunas conducted a study of the effect of temperature changes and found that a variation of 1°C results

TABLE 2
HYDROGEN DIFFUSION COEFFICIENTS IN δ-ZIRCONIUM HYDRIDE

Temperature (°C)	H/Zr	Diffusion Coefficient (cm ² /sec x 10 ⁻⁵)	Precision (%)
652	1.80	0.70	18.2
680	1.70	1.17	15.4
702	—	2.13	5.4
718	1.72	1.89	53.0
718	1.69	2.70	31.1
726	—	3.62	6.0
730	1.72	4.46	8.9
767	1.65	3.00	6.5
778	1.60	2.67	129.0
843	1.54	4.05	13.7
850	1.50	2.76	5.8
899	1.50	5.50	2.5

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in a 2% error in the diffusion coefficient and that this relationship may be linearly extrapolated. Therefore, since variations of 8°C were typical in this work, an error of 16% due to this cause is to be expected. The effect of temperature changes at concentrations near the equilibrium value is particularly detrimental and, in extreme cases, may reverse the direction of the sorption. Therefore, whenever possible, only data taken at less than 90% of the equilibrium concentration were used.

A change of 1% in the radius of the sample leads to a change of 2% in the diffusion coefficient. Since variations in the radius due to addition of hydrogen in the δ region is less than 1%, the error due to such variations will not exceed 2%.

The effect of variations in the pressure of hydrogen on the surface concentration of hydro-

gen is much less than that of temperature variations. At 700°C and 700 mm pressure, a change of 10 mm in pressure results in a change in the surface concentration essentially equal to that resulting from a change of 1° in temperature. Since pressure variations of 10 mm were typical in this work, an error of 2% may be expected in the values of the diffusion coefficients.

The sensitivity of the balance used in this study was 0.5 mg. Since many data points correspond to a change in weight of the order of 10 mg, the error due to the sensitivity should be approximately 5%.

The sum of these errors leads to an expected error of 25% in the diffusion coefficients. The average of the precision values given in Table 2 is 25.7%, indicating that no sources of significant error have been neglected.

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IV. DISCUSSION OF RESULTS

Albrecht and Goode,⁽⁵⁾ Someno,⁽³⁾ and Gelezunas^(1,7) have reported values for the diffusion coefficient of hydrogen in β -phase zirconium hydride (see Table 3). Results obtained by the latter two workers are in good agreement, but are markedly higher than those obtained by Albrecht and Goode who used a permeation technique. The discrepancy may well be due to the sample preparation methods used by Albrecht and Goode. Their samples were prepared from zirconium sheet (maximum thickness, 0.1 mm) fabricated from arc-melted rod; such fabrication methods are very likely to result in the formation of an oxide film. Gelezunas has demonstrated that oxide films, particularly those formed at room temperatures, are extremely tenacious and can be removed only by prolonged heating in vacuum (e. g., 90 min at 927°C). He also showed that such films form a barrier to sorption of hydrogen. Moreover, the dissolution of an oxide film into the thin discs used by Albrecht and Goode would yield a relatively high concentration of dissolved oxygen, since the surface-to-volume ratio of such

samples is very high. Gelezunas showed that oxygen in solid solution with zirconium reduces the rate of hydrogen sorption and that this reduction is related to the effect of oxygen in extending the two-phase, α - β region in zirconium. The greater slope (larger ΔH) reported by Albrecht and Goode may be due to two factors: (1) any oxide film formed during fabrication of the samples will dissolve more readily with increasing temperature, thus reducing its effect as a barrier; (2) the fabrication methods may well lead to the formation of microcracks in the samples and, since the rate of effusion is proportional to $\sqrt{T}$, thus yield incorrectly higher "permeation" rates with increasing temperature. It is reasonable to conclude that the results obtained by Someno and by Gelezunas are probably more nearly correct than are those reported by Albrecht and Goode.

In the AI work, the material used was SNAP fuel material, a 90-10 wt % zirconium-uranium alloy modified by the addition of 0.15 wt % carbon. The study of diffusion in the β -phase of

TABLE 3
DIFFUSION OF HYDROGEN IN THE Zr-H AND Ti-H SYSTEMS

System	Crystal Form	Phase	D_0 (cm^2/sec)	Activation Energy (cal/mole)	Author
Zr-H	B.C.C.	β	5.32×10^{-3}	8,320	Gelezunas ^(1,7)
Zr-H	B.C.C.	β	7.37×10^{-3}	8,540	Someno ⁽³⁾
Zr-H	B.C.C.	β	6.14×10^{-4}	45,900	Albrecht and Goode ⁽⁵⁾
Ti-H	B.C.C.	β	1.95×10^{-3}	6,640	Wasilewski and Kehl ⁽⁸⁾
Zr-H	F.C.C.	δ	5.99×10^{-2}	34,800	Albrecht and Goode ⁽⁶⁾
Zr-H	F.C.C.	δ	-	12,500	Hon ⁽⁹⁾
Zr-H	F.C.C.	δ	1.3×10^{-2}	12,690	This AI work
Ti-H	F.C.C.	α	1.8×10^{-2}	12,380	Wasilewski and Kehl ⁽⁸⁾
Ti-H	F.C.C.	α	-	9,400	Stalinski, et al. ⁽¹⁰⁾

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this alloy was limited to a relatively small temperature range and was performed primarily to test experimental procedures. Results obtained (see Table 1) are in fair agreement with those reported by Someno and by Gelezunas. This agreement indicates that the experimental procedures are satisfactory and that good results might be expected in the study of diffusion in the δ -phase.

The values for the diffusion coefficients of hydrogen in δ -phase fuel are given in Table 2 and in Figure 4. Within the experimental precision, the values are independent of the concentration of hydrogen. Diffusion coefficients were determined for a few samples of pure zirconium and of unmodified fuel; since the values obtained were essentially identical with those observed for SNAP fuel, it is reasonable to conclude that carbon and uranium have negligible effects on the diffusion of hydrogen in the fuel. Hence, the data may be considered equally valid for diffusion in δ -phase zirconium hydride.

If it is assumed that the activation energy, ΔH , required for the diffusion process is independent of temperature, the diffusion coefficient may be expressed by

$$D = D_0 \exp(-\Delta H/RT) , \quad \dots(9)$$

where D_0 is a constant, characteristic of the system.

Least-squares treatment of the data given in Table 2 yields the following expressions for the diffusion coefficient of hydrogen in δ -phase SNAP fuel (equivalent to δ -phase zirconium hydride):

$$D = \left(\begin{matrix} 1.3 & + & 5.8 \\ & & -1.1 \end{matrix} \right) \times 10^{-2} \exp \left[\frac{-(12960 \pm 3440)}{RT} \right] . \quad \dots(10)$$

The standard deviation, σ , of the data is indicated in Figure 4 by the dashed line on each side of the least-squares line and is defined as

$$\sigma = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (D_i - D_i')^2} , \quad \dots(11)$$

where the D_i' are given by Equation 10 and the D_i are given in Table 2.

The authors are unable to account for the considerable scatter of the data. It is unreasonable to attribute the scatter to the small error introduced by the assumption of a constant activation energy (ΔH is not strictly independent of temperature). It is not possible to ascribe the scatter to cracking of the samples, since this did not occur; none of the samples exhibited visible cracks and microscopic examination of several samples yielded no evidence of micro-cracking.

A summary of results obtained for the values of D_0 and ΔH in the zirconium-hydrogen and titanium-hydrogen systems is given in Table 3; data for the latter system are included because the two systems are chemically and crystallographically similar.

It is apparent that the results obtained by Albrecht and Goode are vastly different from those reported by any of the other investigators. Possible causes of this disagreement have been discussed. However, three additional points indicate that the results obtained in this AI work are probably more valid than those given by Albrecht and Goode for δ -phase zirconium hydride.

First, the activation energy, which may be defined as the height of the potential energy barrier between adjacent interstitial positions,

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should decrease with increasing internuclear distance. Thus, the activation energy for a closest-packed structure (e.g., F.C.C.) should be greater than that for a more open structure (e.g., B.C.C.) of the same material. The values given by Albrecht and Goode are in opposition to this rule.

Secondly, for like structures of similar materials, the potential energy barriers between adjacent interstitial positions (hence, the acti-

vation energy) should be similar. The results obtained by all investigations, excepting those of Albrecht and Goode, uphold this dictum.

Thirdly, the results obtained for α -titanium hydride⁽¹⁰⁾ and δ -zirconium hydride⁽⁹⁾ by a completely different technique, nuclear magnetic resonance, agree with the activation energies reported in this AI work and in the work of Wasilewski and Kehl⁽⁸⁾ on titanium hydride.

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