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ATOMICS INTERNATIONAL <small>A Division of North American Aviation, Inc</small>		NAA-SR- TDR NO 9844		APPROVALS	
TECHNICAL DATA RECORD		PAGE 1 OF 10		<i>D. F. Atkins</i>	
AUTHOR R. W. Webb <i>Webb</i>		DEPT & GROUP NO 735-52		DATE 4-27-64	
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		SUBACCOUNT TITLE Coating Development			
		STATEMENT OF PROBLEM			
		ABSTRACT			
		This report is a compilation of hydrogen permeation data through metals. The metals which were considered were those which might be used in the SNAP reactor systems. The permeability of hydrogen through these metals must be known to predict hydrogen mobility and migration in the NaK primary system. Particular concern is for the amount of hydrogen which will migrate into the mercury loop.			
		The flux of hydrogen gas permeating various metals was either determined experimentally or gathered from reports listed in the bibliography. The data were fitted to the following equation:			
		$\phi = \frac{CP^{1/2}}{x} \exp\left(\frac{-Q}{RT}\right)$			
		where			
		ϕ = flux (cc at STP/hr-cm ²)			
		C = permeation constant [$\sqrt{\text{cc(STP)-mm/hr-cm}^2\text{-atm}}$]			
		P = hydrogen pressure (atmospheres)			
		x = membrane thickness (mm)			
		Q = activation energy (cal/mole)			
		R = gas constant (cal/mole - °A)			
		T = absolute temperature			

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I. INTRODUCTION

Objective

The flow of hydrogen through materials represents an important design consideration for hydrogen moderated nuclear reactors. The SNAP reactor systems use zirconium hydride as a moderator material operating between 1200 and 1400°F. The dissociation of this hydride and subsequent hydrogen loss into the liquid metal coolant channels, and eventually the mercury boiler represents a potentially serious problem. Knowledge of hydrogen permeation kinetics through metallic piping could be invaluable in helping to predict migration of hydrogen in the reactor system.

Source of Data

Existing data on rates of hydrogen permeation through constructional materials was reviewed. Obvious gaps (as related to the SNAP project) were filled by experimental studies at AI. As shown in Figure 1, pure metals show a wide range of permeability to hydrogen. Niobium (also palladium) is extremely permeable; whereas, molybdenum and tungsten offer substantial resistance to hydrogen flow. Iron and nickel possess intermediate permeation rates and most of their alloys fall within an extremely narrow permeation range.

Although most metals offer no great potential as hydrogen barriers, proper choice of material could solve problems by offering partial resistance to hydrogen flow or by acting as a "hydrogen window" to dissipate hydrogen gas from specific areas within the reactor system.

General Theory of Permeation

The accepted theory of hydrogen permeation through metals involves the interrelated processes of adsorption, solution, diffusion and desorption.^{1,2,3} Adsorption, the first step in the permeation process, is a very critical step in determining whether or not permeation will occur. A gas which is not adsorbed will not permeate. Normally, adsorption is not the rate controlling step in the permeation process. At extremely low pressures, however, it is quite likely that adsorption does become the rate controlling mechanism.⁴ Usually, rates of sorption and desorption of gases must depend on rates of diffusion

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of the gases through the metal. In the case of diatomic gases, such as hydrogen, adsorption is immediately followed by dissociation of the gas into atoms.

The solubility of gas in metal is also an important consideration in determining if diffusion will occur. This assumption is substantiated² by the fact that there is no known case of a gas diffusing through a metal in which it is not apparently soluble.

Diffusion occurs by a motion of atoms (or hydrogen protons) along interstitial sites. This atomic diffusion process follows from the observation that the rate of diffusion follows the square root of pressure law. Rare gases and polyatomic molecules show no evidence of diffusion through metals. In general, diffusion of gases occurs through the crystal lattice and not along grain boundaries as shown by C. A. Edwards⁴ where he found no difference between the rate of hydrogen diffusion through either single crystal or recrystallized iron.

For most metals, the permeation rate is inversely proportional to the metal thickness, which implies that diffusion is the rate controlling process.

Due to the complex nature and numerous variables in the permeation process, only the total flow of gas through the membrane was measured. The dependence of this permeability on temperature, pressure and membrane thickness is expressed empirically so that a knowledge of these parameters is all that is required for calculating quantities of hydrogen permeating the various metals tested under any conditions.

II. EXPERIMENTAL PROCEDURE

A. Apparatus Used by Other Investigators

A number of distinctly different types of apparatus⁷ have been used by investigators of hydrogen permeability of metals. Of these, the two most commonly used were flat discs and cylindrical tubes. There are obvious advantages and disadvantages to both types, but the author favors use of the cylindrical membrane for several reasons. First, there are generally no welds or seals in the hot zone that may develop leaks. Second, there is no adjoining material which could add to or change the overall flow through the membrane, thereby clouding the results. Third, a much larger testing area can be used which tends to minimize inherent errors due to low flow rates, surface films and impurities. Errors due to thermal gradients are easily compensated for as shown in a later section.

Gas flow rates measured by many investigators referenced herein were observed by allowing the permeating gas to collect in a calibrated volume over a definite time period. A mercury column or a multirange McLeod gauge was used to measure the gas pressure and permit calculation of gas volume per unit time.

B. Apparatus Used in this Investigation

1. Membrane and Furnace System

The apparatus used for this study is shown schematically in Figure 2. The membrane was a thin tube of the material to be tested. The tube may or may not have an end cap welded on as an integral part of the membrane. This depended on the availability of bar stock, the machinability, and/or the weldability of the particular metal being investigated. If an end cap was used, the entire assembly was placed in the isothermal portion of the membrane furnace. In testing tungsten tubing, end seals were accomplished by glass-to-metal seal techniques. The seals were maintained outside the furnace at a sufficiently low temperature so as not to interfere with observed hydrogen flow rates. The main drawback with this arrangement is that a relatively large percentage of the sample is maintained in a non-isothermal condition. Methods

FIGURE 2
PERMEATION APPARATUS

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for correction of this condition will be discussed later.

The membranes tested were generally about 5/8 inch in diameter x 12 to 20 inches long. Wall thickness varied with availability of tubing. The membrane had a 3/16 inch diameter hydrogen inlet tube welded to one end. This further aggravated the temperature gradient problem, since the pressure-probe end must be maintained at less than 700°F to prevent hydrogen loss through the probe walls.

The membrane assembly was placed into a furnace tube of a quartz vacuum system. A resistance wound tube furnace equipped with temperature profile measuring thermocouples surrounded the furnace tube. Hydrogen permeating through the metal membrane was then removed through the vacuum system to a mass spectrometer. This instrument was capable of continuously monitoring the flow of hydrogen gas in the vacuum system.

2. Mass Spectrometer Operation and Calibration

A C.E.C. Model 24-210B helium-hydrogen leak detector was used in these studies. This instrument is capable of sensing hydrogen flows as low as 5×10^{-5} atm cc/hr/div. Hydrogen gas molecules which enter the leak detector flow into the analyzer section where they are bombarded with electrons emitted from an incandescent tungsten filament. The resulting charged particles are then accelerated into a magnetic field where they are separated into groups according to their mass number ($m/e = KB^2/E$),

where

m = mass (a.m.u)

e = number of electrons lost during ionization

B = magnetic field strength

E = accelerating voltage

K = a constant depending on geometry of the instrument.

Measurement of the relative intensities of the groups is accomplished in a DC-amplifier system with the signals

indicated on an output meter.

Hydrogen filled standard leaks (a glass bottle with a small orifice) are calibrated on a McLeod gauge. A three point mass spectrometer calibration was made by observing steady-state flow rates of three different standard leaks. A plot of flow rate vs. meter output resulted in a straight line which passed through zero. If any of the calibration points varied more than 10% from this line, a new McLeod gauge calibration of the standard leaks was warranted.

Using this procedure, the mass spectrometer has been used successfully as an analytical instrument to measure hydrogen flows by the comparative method.

C. Temperature Compensation Techniques

When a metal membrane (tube) is being permeation tested, flow from the membrane follows the basic equation:

$$\phi = \frac{CP^{3/2}}{x} \exp\left(\frac{-Q}{RT}\right)$$

where

ϕ = flux (cc at STP/hr-cm²)

C = permeation constant [$\sqrt{\text{cc(STP)-mm/hr-cm}^2\text{-atm}}$]

P = hydrogen pressure (atmospheres)

x = membrane thickness (mm)

Q = activation energy (cal/mole)

R = gas constant (cal/mole - °A)

T = absolute temperature.

Examination of this equation shows that for any particular test, C, x, Q and R are constants and the measured flow is dependent on 2 parameters; temperature and pressure. If then, pressure is held constant, the flow is only a function of the absolute temperature. If one assumes isothermal conditions, a plot of $\ln \phi$ vs. $1/T$ yields a straight line of slope Q and location constant C. From this, the importance of isothermal test conditions is apparent.

Using the permeation equation, however, one may graphically integrate any test area in a non-isothermal region and assign a weighting factor for flow in that temperature zone. This technique

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uses a series of approximations to arrive at an accurate value.

Recently, a much more sophisticated and reliable method for analyzing permeation data evolved, using a digital computer. The program written for this study by R. F. Berland uses the following logic to compute values for the activation energy of diffusion, Q , (slope of $\ln \phi$ vs. $1/T$ plot):

- 1) Let $\phi_1 = H_2$ flow at T_1
and $\phi_2 = H_2$ flow at T_2
- 2) Let $T_1 =$ temperature gradient along membrane at higher temperature
and $T_2 =$ temperature gradient along membrane at lower temperature
- 3) Using $\phi = \frac{CP^{1/2}}{x} e^{-Q/RT}$ relationship, we divide ϕ_1 by ϕ_2 to obtain

$$\frac{\phi_1}{\phi_2} = \frac{\frac{CP^{1/2}}{x} e^{-Q/RT_1}}{\frac{CP^{1/2}}{x} e^{-Q/RT_2}} \quad \text{which reduces to}$$

$$\frac{\phi_1}{\phi_2} = \frac{e^{-Q/RT_1}}{e^{-Q/RT_2}} \quad \text{or} \quad \frac{\phi_1}{\phi_2} - \frac{e^{-Q/RT_1}}{e^{-Q/RT_2}} = 0$$

- 4) The computer then linearly integrates the temperature profiles T_1 and T_2 and automatically substitutes values of Q into the equation until the equation is satisfied. This method has proven very satisfactory in that only two measured flows are required along with data points on the temperature profile to arrive at an answer.

III. EXPERIMENTAL RESULTS

No attempt was made in this study to verify results of other investigators as related to pressure or thickness dependence on hydrogen permeation. It suffices to say that for all materials tested, pressure dependency followed Sievert's Law:

$$\phi = KP^{1/2}$$

where

$$\phi = \text{flux (cc/hr-cm}^2\text{)}$$

K = proportionality constant

P = upstream H₂ pressure (atm).

Also for most reported results, the permeation process has not shown a dependence on surface effects, which indicates the process is diffusion controlled whereby the flux is inversely proportional to membrane thickness.

Table I is a summary of pertinent data on metals of interest to the SNAP project. Listed are the activation energy for diffusion Q, and the location constant C which are the only necessary quantities for calculating permeation rates under most normal conditions.

TABLE I

$$\phi = \frac{CP^{1/2}}{x} \exp\left(\frac{-Q}{RT}\right)$$

<u>Metal</u>	<u>Reference</u>	<u>Q</u>	<u>C</u>
Hastelloy N	AI	13,800	190
Hastelloy B	6	16,675	1,810
Nickel	1, 2, 5, 8	13,400	1,000
Iron	1, 2, 8	9,100	144
304 Stainless Steel	8	16,100	850
316 Stainless Steel	5, 7	16,075	1,526
321 Stainless Steel	5, 7	16,075	1,526
430 Stainless Steel	7	11,200	360
PH15-7Mo "	AI	20,000	21,600
Haynes 25	AI, 8	15,100	327
Molybdenum	2, 5, 8	20,100	950
Tungsten	AI, 8	29,340	1,840
Niobium	8	3,430	1,040
Platinum	1, 2	18,600	1,840

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FIGURE 1

HYDROGEN PERMEATION
VS.
TEMPERATURE

*Read for Nb

IV. SUMMARY AND CONCLUSIONS

The experimental data are summarized in Figure 1, which shows a plot of flux (cc/hr-cm^2) of hydrogen through various metals as a function of temperature. All the data shown are for 1.0 atmosphere hydrogen pressure differential and 1.0 mm membrane thickness.

It is interesting to note from data displayed in this manner that for the pure metals (alloys excepted) which do not hydride, the hydrogen permeation rate decreases as a function of absolute melting temperature of the metal. Or, stated differently, the hydrogen flux through pure metal is essentially constant at a constant ratio of the melting points of those metals. Also, it becomes a distinct possibility (as deduced from the above data) that the activation energy for diffusion for non-hydride forming metals is a constant with respect to a constant ratio of absolute melting temperature.

Table II shows value for such a comparison computed at one-third the absolute melting temperature of four different metals.

TABLE II

<u>Metal</u>	<u>Melting Point ($^{\circ}\text{K}$)</u> <u>T_m</u>	<u>Activation Energy</u> <u>Q/T_m</u>	<u>H_2 Flux</u> <u>$\bar{Q}/T_m/3$</u>
Nickel	1726	7.6	1.1×10^{-2}
Iron	1810	6.0	2.1×10^{-2}
Molybdenum	2873	7.3	1.7×10^{-2}
Tungsten	3653	8.0	1.0×10^{-2}

Garner⁹ has stated that lattice mobility relations are governed by or tend to become operative at temperatures which represent fairly constant fractions of the absolute melting-point of the solid. Such "characteristic temperatures" are only a general guide to solid state diffusion, but as such they are useful.

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