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HYDROGEN PERMEATION RESISTANT LAYERS FOR LIQUID METAL REACTORS

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J. C. McGuire

March 1980

American Nuclear Society Symposium
"Tritium Technology in Fusion
and Isotopic Applications"

April 29-May 1, 1980

Dayton, Ohio

HANFORD ENGINEERING DEVELOPMENT LABORATORY
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HYDROGEN PERMEATION RESISTANT LAYERS FOR LIQUID METAL REACTORS

J. C. McGuire
Hanford Engineering Development Laboratory

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INTRODUCTION

Tritium is generated in both fission and fusion reactors. Although most of the tritium in a liquid metal cooled fission reactor is trapped in either the primary or the secondary cold trap,⁽¹⁾ tritium control is still a matter of environmental concern. The tritium inventory in a fusion reactor will far exceed that of its fission counterpart, therefore, permeation through containment walls and exposed surfaces must be minimized. Savage and Strehlow⁽²⁾ have shown that tritium permeation rates through metals do not adhere strictly to the half power pressure law. They also report the usefulness of an oxide layer on stainless steel as a permeation barrier.

Reviewing the literature in the tritium diffusion field one can readily see a wide divergence in results for both the response of permeation rate to pressure, and the effect of oxide layers on total permeation rates. We have investigated the basic mechanism of protective oxide layers and have developed two coatings which are less hydrogen permeable than the best naturally occurring oxide. The work to be described was part of an HEDL-ANL cooperative research program on Tritium Permeation in Liquid Metal Cooled Reactors. This included permeation work on hydrogen, deuterium, and tritium with the hydrogen-deuterium research leading to the developments to be described.

EXPERIMENTAL

We carried out hydrogen-deuterium permeation research in the pressure range 13-1300 Pa (0.1 - 10 torr) using a glass vacuum-line of the design shown in Figure 1. This was a simple permeation measurement system

SCHEMATIC OF HYDROGEN/DEUTERIUM PERMEATION SYSTEM

FIGURE 1

HEDL 7802-113.4

containing a diffusion membrane and associated tubing whose total volume had been calibrated. The calibrated volume contained a three range capacitance manometer and digital readout. The type 304 stainless steel diffuser was 91 cm (36") of 0.32 cm (0.125") O.D. tubing with 0.4 mm (0.015") wall. We wound this tubing on a mandrel to obtain the short compact coil shown in Figure 2. Surface area of the diffuser was 50 cm².

Mechanical fittings connected the coil to two penetrations in the fused silica heater chamber. The interior of the diffuser coil was a part of the small calibrated volume containing the capacitance manometer. Total volume in the pressure measurement system was less than 50 cm³. Therefore, any pressure change of 0.13 Pa (0.001 torr) represents 6.5×10^{-5} cm³(STP) or 1.3×10^{-6} cm³ per cm² of diffuser area. The diffuser was heated by a tubular-resistance furnace. Permeation studies were made over the range 350-750°C with emphasis on the 350-550°C temperature range.

In operation, hydrogen or deuterium permeated through the diffuser into the calibrated volume to the required starting pressure, usually 1300-1560 Pa (10-12 torr). This step eliminated contaminants and ensured purity of the starting gas. Total leakage rate in the system with the spiral diffuser chamber at 550°C was 2×10^{-9} cm³/sec (5×10^{-6} torr-liter/hr) attributable to helium diffusion through the Pyrex walls of the diffuser connections.

Early experiments established the following:

1. In the pressure range 13-1300 Pa (0.1-1.0 torr) H₂ and D₂ permeation rates were nearly linear with changes in pressure.
2. Very clean membranes exhibited half power pressure dependence over a wider pressure span than oxidized materials.
3. Hydrogen and deuterium permeation rates through 304 stainless steel showed permeation dependence on the $\frac{1}{\sqrt{M}}$ law as expected.

We first decided to determine, if possible, the reason for the wide variation in the reported effect of oxide layers on hydrogen permeation rates. We considered oxidation temperature to be a possible factor, and found

TYPICAL DIFFUSION MEMBRANE

FIGURE 1

that a membrane oxidized for 200 hours at 750°C had 20 times lower permeation rate than one oxidized for 750 hours at 550°C. Auger Microprobe Analysis shown in Table 1 revealed that the surfaces created by the two oxidation treatments were entirely different. The specimen treated at 750°C had a high concentration of Mn, Cr, and O within the first 2000 Å of surface whereas the 550°C specimen had only Fe and O in the same area. Savage⁽²⁾ had identified the Mn/Cr/O complex as a permeation resistant layer and investigations at HEDL found this material on outside surfaces of sodium loops after operating at 500-600°C for 6000 to 24000 hours. Therefore, the material can be formed at lower (550°C) temperatures but formation takes much longer.

As-received stainless steel appears to have a hydrogen permeation resistant barrier in the form of islands of chromium carbide in a thin but almost continuous layer. This layer can be destroyed by contact with air at 550°C. Figure 3 shows the sharp increase in permeation rate which reverses within 20 hours, followed by the usual gradual decay as the long term permeation resistant oxide layer is formed.

The dispute over "clean" surfaces is academic in view of the conditions encountered in operating liquid metal cooled fission or fusion reactors. In operating reactors, surfaces exposed to air or reactor containment gas (99% N₂, 1% O₂) are not clean. By the time a reactor achieves full temperature operation all external surfaces act as barriers to tritium permeation to some degree. The only surfaces which will exhibit classical predictable diffusion characteristics will be the Intermediate Heat Exchanger (IHx) tubes in contact with liquid metal on both surfaces. In this case tritium in primary sodium or lithium can be transferred to secondary liquid metal at rates two orders of magnitude faster than those seen in liquid metal/membrane/vacuum or liquid metal/membrane/gas transfer.

The external surface of the reactor vessel and piping may still require more permeation protection than the oxide layer provides. In a fission reactor even where tritium inventories in the sodium are low, containment permeation protection is needed until the natural oxide layer can be built up

TABLE 1
#1 & #2 DIFFUSER
COMPARATIVE AUGER ANALYSES

DEPTH Å	%O ₂		%Cr		%Mn	
	750°C	550°C	750°C	550°C	750°C	550°C
50	8.13	7.07	16.46	0	14.24	0
200	7.26	6.11	27.42	0	16.80	0
500	6.61	6.20	36.06	10.05	18.64	0
2000	8.01	4.73	46.69	13.45	20.49	0
7500	7.24	.61	47.06	16.98	14.26	0

	%Fe		%Ni	
	750°C	550°C	750°C	550°C
50	39.84	67.17	4.49	17.15
200	35.65	69.74	3.56	16.48
500	23.79	65.83	2.71	12.54
2000	17.22	63.53	3.24	13.56
7500	23.24	64.96	4.69	14.59

HEDL 7605-78.2

FIGURE 3. Variation of Hydrogen Permeation Rate With Time for a 304 SS Diffuser Exposed to Air at 550°C.

at the low (550°C) operating temperatures. In a fusion reactor proposed liquid metal heat transfer fluids such as sodium or NaK and tritium breeder blankets may be handling much higher tritium inventories at the significant partial pressures necessary for tritium recovery. In this case extra external permeation protection will be necessary.

We have developed an external coating for reactor containment and tritium processing equipment which is inexpensive, simple and which can be applied after the reactor and equipment have been assembled.

Liquid phosphoric acid (H_3PO_4), with additives to decrease surface tension and ensure wetting, can be applied to the exterior surfaces by brushing, dipping, or spray painting. It is fired in place at 350°C or more by the heat of the reactor. Exposed to air or 99% N 1%O this surface forms a phosphate glass which is 10 times less permeable to hydrogen/tritium than the best oxide layer. It also reacts with the outer containment surface, bonds completely and prevents subsequent surface oxidation of the coated material. A coated surface fired in air at 550°C for 600 hours retained its shiny metallic appearance as seen in Figure 4. The coating was a good electrical insulator. Even when intentionally flaked away, the surface area resists Auger Microprobe analysis because it is a non-conductor. The coating is formed in and is stable in air. Sharp thermal cycling can result in an increase in hydrogen permeation rate but at reactor operating temperature the microcracks formed by thermal cycling are resealed and permeation resistance is restored. At temperatures above 450°C the phosphate glass is semi-fluid, therefore, the self healing process is automatic.

Coating is desirable which will be effective in preventing tritium transfer between the primary and secondary systems of a reactor. This is of particular interest in fission reactors preventing tritium release from fuel and control pins, and migration from primary to secondary systems. The phosphate glass is stable in air but unstable in liquid metals, therefore another coating is necessary.

PHOSPHATE GLASS (LEFT) AND NORMAL OXIDE
BOTH RUN 600 HRS @ 550°C IN AIR

FIGURE 4

Although pure aluminum is not compatible with molten alkali metals, early work (3) showed that aluminum applied to a nickel-chromium stainless steel or a nickel alloy can result in a surface coating of nickel aluminide. DeVan⁽⁴⁾ found that this layer on austenitic stainless steel or high nickel alloys forms a corrosion- and wear-resistant layer in lithium at 500°C. Johnson, et al,⁽⁵⁾ have shown the nickel aluminide layer to be the most resistant to sodium corrosion at temperatures up to 650°C. Nickel aluminide has been used for some time as a corrosion- and wear-resistant layer on turbine blades in aircraft. We have found that the aluminide layer is the most effective hydrogen permeation layer for austenitic stainless steel. As shown in Figure 5 the aluminide layer is two orders of magnitude more permeation resistant than the best oxide layer.

An aluminide layer can be formed by at least three techniques.

1. Pack vapor treatment in a hydrogen atmosphere at 800-1000°C.
2. Dipping in molten aluminum or sodium-aluminum at 800°C.⁽³⁾
3. Formation in situ by adding 5% Al to the lithium in a circulating system at + 500°C.⁽⁴⁾

In each case the aluminide coating is in the form of a duplex layer approximately 40 μm (1.5 mils) thick. The outer layer is approximately 20 μm thick and is more aluminum-rich than the inner layer. On an austenitic stainless steel both layers contain Fe, Cr, and Mn, as well as Ni, Al.

CONCLUSIONS

There is a basic difference in permeation rate and structure between the oxide coatings formed on austenitic stainless steel at 550°C and at 650°C. Two types of hydrogen permeation resistant coatings have been developed for use with both fission and fusion reactors. An external coating consists of H_3PO_4 applied by painting techniques. This coating is fired

FIGURE 5

in place as a semifluid glass. It is compatible with air, and reactor containment atmospheres such as 99%N₂-1%O₂. It cuts hydrogen permeation rates of oxide coatings by a factor of 10.

A coating of nickel aluminide formed on austenitic steels and high nickel alloys is resistant to attack by hot sodium and lithium. The layer has the lowest permeation rate for hydrogen/tritium of any material tested.

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