Final Report

MASTER

THERMACORE, INC.
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INVESTIGATION OF NON-MAGNETIC ALLOYS FOR THE SUPPRESSION OF TRITIUM PERMEATION

Prepared for:

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DISCLAIMER

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1. EXECUTIVE SUMMARY

This report describes a small (300 man hour) literature survey relating to the suppression of tritium loss by permeation through the walls of fusion reactors. Such loss constitutes a serious potential environmental hazard. Unless reduced to low levels, leakage of tritium into the ecological system would seriously limit the public acceptance of fusion reactors.

The program was based on prior in-house Thermacore work to suppress hydrogen permeation into high temperature (800 C) heat pipes. The Thermacore approach involves selection of a steel with a small (.5 to 5%) aluminum content. The aluminum is diffused to the surface and oxidized. The resulting alumina layer has low hydrogen permeation. The approach has been validated by permeation measurements at Argonne National Laboratory. Permeation through this alloy was 150 times lower than though conventional steels.

The present work was aimed at identification of alloys which might combine low tritium permeation with other properties desired in fusion reactor vessels, heat exchangers, lithium-handling plumbing and other components likely to contain tritium. These properties include low radiation damage, low magnetic permeability, high temperature strength, and compatibility with potential heat transfer and blanket materials.

The work consisted of two tasks: Problem Definition, and Literature Search and Analysis. Task I was complicated by the incomplete status of fusion reactor development, particularly with respect to selection of coolant and blanket materials and temperatures. The approach taken was to establish a probable range of requirements. In Task II, the literature was searched for materials data which was applicable to this range of requirements.

It was concluded that non-magnetic steels can be made which will have the desired properties of low permeation and high temperature strength. Life in contact with heat transfer and blanket materials will depend on final selection of these materials and the operating temperatures chosen. At worst, the steels with low tritium permeability appear to have compatibilities at least equal to the high permeability steels presently under consideration. The results of the study appeared to be highly promising. It is recommended that the work be continued in two paths: an effort to define the physical process by which the alumina-coated steels suppress permeation and a parallel effort to produce and test small samples of the more promising steel alloys. Test data on the steels will be useful in investigating the permeation mechanism. The mechanism study will help to pin point the most promising alloy compositions.

2. INTRODUCTION AND BACKGROUND

The loss of tritium from fusion reactors represents an important potential environmental hazard. In addition to the possibility of actual leaks from tritium-handling systems, there is the problem of permeation. All metals are rapidly permeated by hydrogen species at projected fusion reaction vessel temperatures ($\approx$ 550 C), as shown by the earlier data of Smithels and Ransley,[1] Waldschmidt[2] and Turnbull, et al[3]. Iron alloys are considered to be the most probable construction materials for tritium-handling. These alloys are particularly susceptable to permeation as shown in Figure 1, which summarizes the pertinent early German data from Reference 2.

It has been shown in Waldschmidt[2], Turnbull[3], Eastman[4], and Eastman and Fox[5] that hydrogen permeation through certain non-metallics is lower than through metals by several orders of magnitude. Ceramic materials may be the leading candidates for suppression of tritium permeation from fusion reaction vessels.

It does not appear to be practical to consider fusion vessels made of free-standing ceramics. Therefore, a promising approach to the construction of a reaction vessel and associated tritium-handling hardware may be an iron alloy with a ceramic coating. This program is concerned with the exploration of a means of achieving that end result.

For several years Thermacore has maintained an in-house program to investigate means of suppressing the permeation of hydrogen into high temperature ($\approx$ 800C) heat pipes. Considerable success has been achieved. A class of aluminum-steel alloys has been identified as having unusually low permeation rates when properly processed.

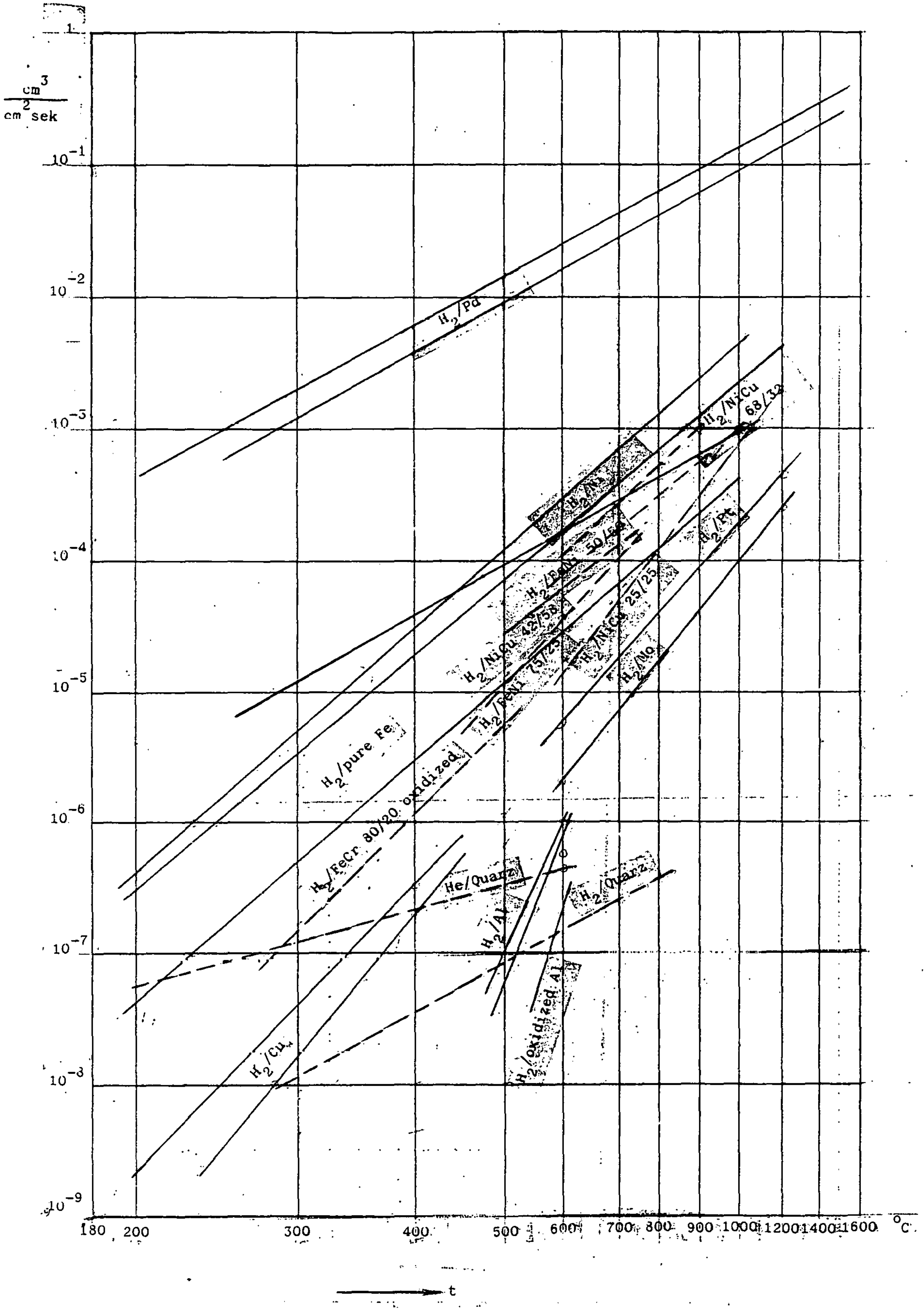

FIGURE 1

Gas Permeation of Various Materials
(Waldschmidt[2])

KEY	REVISION NC

A conversation with DOE Magnetic Fusion personnel in 1976 brought to light the need for suppression of tritium permeation from fusion reactors. A sample of the Thermacore material was tested at Argonne National Laboratory. The results showed a reduction in hydrogen permeation by a factor of roughly one hundred fifty when compared with more conventional steels.[6,7]

The basic Thermacore process is described in U.S. Patent #4,082,575. The procedure starts with selection of a steel which contains a small quantity of aluminum as an alloying element. The aluminum content is typically 0.5 to 5%. The aluminum is diffused to the surface and oxidized there. With careful cleaning, a continuous ceramic layer is formed on the surface. Thickness is typically 1-2 micrometers. Adherence to the substrate is excellent. The coating is self-healing in that if scratched, it can be reformed by heating in air.

The present contract followed an unsolicited Thermacore proposal to extend the previous work to fusion reactor requirements.

3. DESCRIPTION OF TECHNICAL WORK

The purpose of the program was to study means of suppressing tritium permeation from fusion reaction vessels and components, building on technology previously developed at Thermacore for the reduction of hydrogen permeation into heat pipes.

3.1. Objective

The objective of this program was to identify candidate alloys which have the properties desired for a fusion reactor vessel: non-magnetic, high temperature strength, liquid metal compatibility, the lowest possible rate of tritium permeation and resistance to nuclear radiation.

3.2. Program Organization

The program consisted of two tasks:

Task I - Problem Definition. The first portion of the effort was devoted to an attempt to define the requirements of a fusion reactor vessel and its associated heat transfer plumbing. These were identified as the principal components subject to substantial tritium concentrations.

Task II - Literature Search and Analysis. This task represented the bulk of the work and was devoted to the search for information on hydrogen permeation through metals, glasses and ceramics as well as identification of alloys having the potential for low tritium permeation.

The investigation was carried out principally by Dr. John C. Turnbull (permeation through non-metals), Mr. S. William Kessler, Jr. (permeation through metals and metallurgy of candidate alloys) and Mr. G. Yale Eastman (permeation through coated metals). Dr. Turnbull and Mr. Kessler were consultants to Thermacore. Mr. Eastman was the

Thermacore Program Manager.

3.3. Task I - Problem Definition

An effort was made to define the requirements of a fusion reactor vessel and its associated plumbing. Sources consulted included professional personnel at DOE, Argonne National Laboratory, Oak Ridge National Laboratory, University of Wisconsin and North Carolina State University. It was concluded from these discussions that the requirements are a moving target as yet and will remain so for several years until the first full scale tests are conducted. In addition, the requirements vary appreciably from the reaction vessel itself through the plumbing to the heat exchangers. The situation is compounded by the fact that five heat transfer systems are still under consideration.

It was, however, found to be possible to establish a range of requirements against which candidate materials could be judged. This approach is adequate at the present stage of investigation. It was recognized from the start that the first generation of reactor test equipment will be built before the results of the present investigation could be put to work. Therefore, the required performance will be further refined by experience and the present approach to requirements is justified by the developmental status of the overall fusion program.

It is desired to operate the first wall and its associated cooling loop at the maximum temperature permitted by materials constraints in order to maximize thermal-to-electric conversion efficiency (Carnot). A number of cooling methods are under consideration for controlling first wall temperature and delivering the generated energy to the conversion system.[8] These include water, steam, gas (helium), liquid metal (Li and Li/Pb) and molten salts. Each has its effect on the system thermal requirements. The temperatures range from 300 to 600 C.

In most designs the reactor is surrounded by a lithium-containing blanket in which tritium is bred. An appreciable amount of the total heat is produced in the blanket. Therefore, the blanket, also, must be cooled and the tritium separated. Low tritium permeation is required of this plumbing as well as the first wall cooling system. In those approaches in which lithium or Li/Pb alloys are used as blanket materials, these may also serve as coolants.

Thus, the thermal requirements cannot be pin pointed until the cooling method is chosen. However, for the purposes of the present study it was deemed sufficient to look qualitatively for materials which have high strengths and low tritium permeation rates in the 300-600 C temperature range.

Each candidate cooling and blanket approach has its peculiar compatibility requirements. Several, which otherwise are potentially severe, are ameliorated by a willingness to consider replacement of major portions of the containment hardware on a two year cycle. Therefore, systems which might otherwise be inappropriate (e.g., lithium with nickel-iron alloys) may be feasible.

The Thermacore approach to suppression of permeation involves in situ formation of a thin (1-2μ) ceramic layer on an underlying substrate. High sputtering rates within the fusion reaction vessel[8] make the use of this approach inappropriate on the inside of the first wall. Aluminum oxide is the principal constituent in the suppressive layers developed by Thermacore. The rapid attack of Al_2O_3 by high temperature liquid lithium makes the approach of doubtful merit in those portions of the system where hot lithium may be used. In both the sputtering and Li contact situations, however, the attack may be limited to one side of the container. A coating on the opposite side may serve to suppress permeation. In this condition there is the possibility of an internal build-up of hydrogen pressure that might damage the coating integrity.

The intensity and character of nuclear radiation is expected to vary widely at different locations within a fusion machine. The behavior in this environment of thin ceramic films on metallic substrates is unknown. Irradiation tests will be required to establish the effects.

3.4. Task II - Literature Search and Analysis

The literature was first examined for data on the permeation process and then on specific findings in metals, non-metals and ceramic coated metals. This was followed by an examination of the process of forming alumina layers on steels and a brief review of the literature pertinent to the compatibility with lithium of alumina coated steels.

3.4.1. The Permeation Process in Various Materials

3.4.1.1. Permeation Definition

Permeation: Permeation of a gas through a metal is the overall process of moving of the bulk gas phase on one side of the metal wall through the metal to the bulk gas phase on the other side. This process consists of interactions at both the entry and the exit surfaces of the metal, as well as the actual transport through the metal. The diffusion of the gas through the metal is a term applying strictly to the means of transportion. To permit gas movement through the metal there must exist a solubility of the gas in the metal.

Small amounts of dissolved hydrogen and its radioactive forms, tritium and deuterium, have a marked effect on the physical properties steel. As little as 1 ppm may have a significant effect and cause the delayed cracking of steel under a sustained load. In the construction of a nuclear fusion reactor, the permeation of tritium and deuterium must be a minimum to prevent the escape of these gases to the environment. Permeability, P is defined by:

$$J = -P/\Delta x$$

where J is the diffusion current per unit area and Δx is the thickness of the metal. Permeability is related to the diffusion coefficient by

$$J = -D\frac{(C_1 - C_2)}{\Delta x}$$

where $(C_1 - C_2)/\Delta x$ is the concentration gradient in the metal wall. Since the concentration of hydrogen in the steel is proportional to the square root of the pressure, P, the permeability may be defined as

$$J = \frac{-P, \; p_1^{1/2} - p_2^{1/2}}{\Delta x}$$

where p_1 is at the high pressure side and p_2 is at the low pressure side of the specimen.

Permeability is dependent upon temperature, the nature of the metal, boundary conditions, and thickness of the metal. Since there are multiple steps involved in permeation, and the boundary conditions are difficult to define, there is sometimes poor agreement between the results of different investigators.

Dodge[10] gave the following equation for expressing the effect of pressure and temperature on permeation.

$$J = \frac{K}{x} (p_1^{1/2} - p_2^{1/2})\, e^{-E/RT}$$

K is a constant that depends on the metal and probably on several factors related to the state of the metal, E is the activation energy, R is the gas constant and T is the absolute temperature.

For permeation through a thin walled tube of iron, Smithells and Ransley[1] found the following relationship for hydrogen:

$$P = 1.63 \times 10^{-3} p^{1/2} e^{-4800/T}$$

and Borelius and Linblom[11] obtained

$$P = 1.60 \times 10^{-3} p^{1/2} e^{-4700/T}$$

The pressure was measured in mm of Hg and the temperature in degrees Kelvin.

Permeability is related to solubility, S, and diffusion, D, by

$$P = S \cdot D$$

3.4.1.2. Solubility

Only small quantities of hydrogen are soluble in iron and the amount increases with increasing temperature. The solubility also varies with the square root of pressure (Sieverts' law) above 400°C, and has a positive temperature coefficient which corresponds to a negative heat of absorption.[12]

Hydrogen enters the iron in a dissociated form, rather than as molecules, and is dissolved and diffused in the iron interstitially.

It is uncertain whether the form is an atom or a proton. The extremely rapid diffusion rate of hydrogen in iron has led some to speculate that the dissociated particles are protons which have an extremely small radius (10^{-5} Å)[13].

The best equation[14] describing the solubility of hydrogen in α - iron at temperatures greater than 400°C is

$$S(\text{ppm}) = 42.7\ p^{1/2} e^{-3280/T}$$

Armbruster[15] determined the solubility of hydrogen in iron, nickel and 13 steels of varying compositions. The samples are listed in Table I and range in structure from ferritic to austenitic. The solubility of hydrogen in these steels falls into three groups: 1, the ferritic low in alloying elements, 2, an intermediate group high in alloying elements, and 3, the austenitic structured alloys. The solubility of hydrogen in the austenitic alloys is several times as great as the ferritic alloy group. The addition of a small amount of Al did not affect the solubility of hydrogen in the ferritic alloy group. From this data it can also be concluded that larger amounts of hydrogen can be dissolved in the face centered cubic austenitic

TABLE 1

	Material	Composition								Solubility Micromole/100 g at 1 mm			Heat of Solution
		C	Mm	S	P	Si	Cr	Ni	Other	$400^{o}C$	$500^{o}C$	$600^{o}C$	Cal/g-mole
1	Carbonyl iron	0.011	–	–	–	–	–	–	–	0.60	1.16	1.93	13300
2	Mild steel	0.39	0.73	0.032	0.022	0.19	0.048	0.12		0.45	0.97	1.58	14200
3	Mild steel	0.39	0.70	0.049	0.016	0.128	–	–		0.79	1.29	2.18	13600
4	Mild steel	0.12	0.47	0.041	0.016	0.003	–	–		0.69	1.35	2.15	13100
5	Mild steel	0.10	0.39	0.032	0.015	0.007	–	–		0.45	1.00	1.79	16200
6	1.5% Mm steel	0.20	1.46	0.022	0.027	0.205	–	–		0.58	1.21	2.07	14800
7	3% Si Steel	0.05	0.23	0.013	0.010	3.17	–	–	Al 0.27 Al_2O_3 0.03	0.46	1.52	2.42	18600
8	4% Ni Steel	0.32	0.64	0.020	0.023	0.245	–	3.64		0.50	1.09	2.02	16200
9	13 Cr .3 C ferritic	0.32	0.47	–	–	0.28	12.78	–		0.33	0.73	1.46	16400
10	16% Cr Steel	0.09	0.46	0.014	0.012	0.395	15.60	0.33		0.40	0.84	1.56	15900
11	28% Ni steel	0.025	0.18	–	–	0.06	–	27.88		1.51	2.44	3.54	9700
12	13% Mm steel	1.40	12.98	0.019	0.048	0.32	–	–		1.63	2.54	3.25	8000
13	13 Cr .3 C austenitic	0.32	0.47	–	–	0.28	12.78	–		4.37	5.20	6.18	4200
14	18 Cr-18 Ni steel	0.07	0.37	0.005	0.006	0.47	18.30	9.92		5.24	6.37	7.55	4300
15	Nickel	0.13	0.13	–	–	0.04	–	99.52	Cu 0.06 Fe 0.09	5.93	7.94	9.83	5900

steels than in the body-centered cubic ferritic steels.

The solubility of the hydrogen isotopes has also been studied. Sievert et al found the solubility of deuterium in iron to be a little less than that of hydrogen, and the difference increased with increasing temperature. Hawkins[16] compared the solubility of hydrogen, deuterium, and tritium in a austenitic stainless steel (18.8 Cr, 10.66 Ni) at temperatures in the range from 300 to 750°C at pressures of 0.1 to 2.5 mm of Hg. The solubilities were given in the following form:

$$\text{Log } S = -\frac{A}{T} + B$$

where S is the solubility in micromoles per of 100 gm of steel at 1 mm of Hg and T is degree Kelvin. The experimental values were as follows:

Isotope	A	B	H Cal/Mole
Hydrogen	366.9	1.314	3370
Deuterium	382.2	1.259	3520
Tritium[a]	400.2	1.267	3680

(a) T = 96%, H = 4%

The solubility of hydrogen in steels no longer obeys Sieverts' law

$$S = k\,(P_{H_2})^{\frac{1}{2}}$$

at temperatures less than 400°C. At temperatures less than 400°C the solubility deviates markedly from the extrapolation of higher temperature data in the direction of greater solubility.[17] This experimentally observed abnormally high solubility of diffusible hydrogen below 400°C tends to confirm the hypothesis of lattice traps for the hydrogen atoms. Since the number of sites for traps increases with cold working, a greater amount of hydrogen can be dissolved in cold worked steel.

Hydrogen Entry: Hydrogen can enter steel in numerous ways. The following is a list of the commonly accepted methods of charging steels with hydrogen:

1. Pickling
2. Corrosion, such as rusting
3. Electroplating
4. Grinding using water as the coolant or moisture in the air
5. Hydrocarbon lubricants
6. Paint strippers
7. Sulfide corrosion of steel
8. Breaks in protective coatings such as Cd, Zn, Fm or Al which are more anodic than the steel.
9. Cathodic protection

None of these methods are applicable to intended use as a reactor vessel but should be considered as potential sources of hydrogen in fabricating the vessel.

Effects of Surface Treatment and Environment: If the entry of hydrogen, rather than diffusion, is the controlling factor in permeation of hydrogen through steel, as appears to be the case under most conditions, then variations in the nature of the steel surface will influence the permeation.

Smithells and Ransley[1] studied the effect of surface treatment on iron and nickel. The results are summarized as follows:

TABLE 2

Treatment	Temp °K	H_2 Pressure mm of Hg	Hydrogen Permeation $cm^3/sec/cm^2$ (a)
Polished	673	0.77	$.47 \times 10^{-7}$
Etched	673	0.77	4.4×10^{-7}
Polished	863	0.073	1.28×10^{-7}
Oxidized and reduced at 600°C	863	0.073	0.76×10^{-7}
Further reduced at 800°C	863	0.073	1.54×10^{-7}

The oxidation was done by introducing a small amount of oxygen into the permeation equipment and heating the sample to form a thin oxide film. At 600°C there was only a partial reduction of the oxide. Such an oxidation and reduction treatment doubled the hydrogen permeation rate of nickel as compared to a polished surface. Etching the iron's surface with acid had the greatest effect, increasing the permeation rate by a factor of 10.

3.4.1.3. Diffusion and Permeation

The entry and diffusion of hydrogen in metals occurs as atoms dissociated from the molecule, or as positively charged ions (protons). The molecule of hydrogen, H_2, does not diffuse in metals nor do the molecules of other diatomic gases.

The driving force for diffusion of hydrogen in steel can either be a hydrogen concentration gradient or a stress gradient. As an example, in a sample charged uniformly with hydrogen, the hydrogen can diffuse to a region of maximum stress just in front of a crack tip in a part under load. The diffusion rate of hydrogen does not change rapidly with temperature. Sykes, Burton and Gegg[18] calculated the diffusivity, D, for iron as listed in Table 3. The results are compared to the permeability results of Bermek and Klotzback[19] for a Ni-Cr-W steel. Over the temperature range of 300 to 600°C the diffusivity changed by only a factor of 2 while the permeability changed by a factor of 20. Thus, the major factor in increasing the permeability is the increase in solubility with increasing temperature.

The following equations have been determined by various investigators to define the rate of diffusion:

$$D = .0022e^{-2914/Rt}$$

by Geller and Sun[20]

$$D = 8.8 \times 10^{-4} e^{-3050/RT}$$

by Stross and Tompkins[21] for the temperature range of 150 to 900°C and

$$D = .0014e^{-3200/RT}$$

by Johnson and Hill[22] for temperatures greater than 200°C.

At low temperatures investigators report diffusion coefficients at 25°C ranging from 1×10^{-9} to 1×10^{-5} cm^2/sec; these values differ by a factor of 10,000.

Pressure does not appear to have any effect on the rate of diffusion. Bardenheuer and Thankeiser[23] have shown that hydrogen will diffuse in steel against a back pressure of molecular hydrogen of 300 atmospheres, the limit of their equipment.

Crystal structure has an effect on the rate of diffusion. Hydrogen will diffuse through the more open body-centered cubic structure of alpha iron more rapidly than the face-centered cubic structure of gamma iron. The equations for the diffusion coefficients are:

iron $D = .0022e^{-2914/RT}$

iron $D = .0107e^{-9944/RT}$

according to Geller and Sun.[20]

Sykes, Burton and Gegg calculated the diffusivity of hydrogen in austenite using Sieverts' solubility data. The results of their calculations are shown in Table 4 which should be compared to the data for ferritic steel in Table 3.

TABLE 3

Temperature °C	Diffusivity D sq cm/sec	Permeability N(a)
20	1.5×10^{-5}	-
100	3.5×10^{-5}	0.00026
200	6.7×10^{-5}	0.0045
300	1.00×10^{-4}	0.029
400	1.38×10^{-4}	0.11
500	1.70×10^{-4}	0.26
600	2.04×10^{-4}	0.59
700	2.34×10^{-4}	1.00
800	2.69×10^{-4}	-

(a) N is the number of cc of gas at NTP diffusing through 1 pq cm of a plate 1 mm thick in 1 hour at a pressure of 1 atm.

TABLE 4

Temperature °C	Diffusivity cm^2/sec	Permeability vol/hr
800	6.0×10^{-5}	.55
900	8.7×10^{-5}	1.2
1000	1.3×10^{-4}	2.4
1100	1.9×10^{-4}	3.9
1200	2.5×10^{-4}	6.5

The steel composition can affect the diffusion of hydrogen. Geller and Sun[20] reported that additions of silicon, chromium and nickel decreased the diffusivity of the alpha and gamma modifications of iron. At room temperature the evolution rate of hydrogen from supersaturated samples of a 4.33 percent silicon steel was much less than a 25.37 chromium iron alloy. The diffusion coefficients for a number of steels are tabulated in Table 5. Hobson[24] observed very low diffusion rates for a 14% Cr, ferritic stainless steel. At 100°C, the diffusion coefficient was 3.2×10^{-7} cm^2/sec for the stainless steel compared to 1.34×10^{-5} for a 2½ Ni-Cr-Mo steel.

TABLE 5

Steel Composition	Temperature °C		
	400°C	600°C	800°C
Pure α iron	2.5×10^{-4}	4.0×10^{-4}	5.9×10^{-4}
Fe with 1.06% Si	8.3×10^{-5}	1.8×10^{-4}	2.9×10^{-4}
Fe with 1.85% Si	5.1×10^{-5}	1.3×10^{-4}	2.2×10^{-4}
Fe with 3.11% Si	2.1×10^{-5}	7.4×10^{-5}	1.6×10^{-4}
Fe with 4.33% Si	9.3×10^{-6}	4.8×10^{-5}	1.3×10^{-4}
Fe with 27.45% Si	3.2×10^{-5}	9.1×10^{-5}	1.7×10^{-4}
Pure γ iron	6.3×10^{-6}	3.8×10^{-5}	1.0×10^{-4}
γ Fe with 18% Cr 8.9% Ni	1.1×10^{-6}	1.1×10^{-5}	5.0×10^{-5}

Chang and Bennett[71] studied the effect of Cr, Ni, and Mo on the rate of hydrogen permeation in iron. They found that Cr had little effect on the permeation in γ iron, but greatly reduced the rate of permeation in α iron. Nickel and molybdenum had little effect. Permeation in an Fe-4.25 Cr alloy was less than one-tenth the rate observed for Armco iron over the temperature range of 400 to 750°C.

Carbon also affects the diffusion of hydrogen in iron. Bhat and Lloyd[25] observed that increasing the amount of carbon reduced the permeation rate of hydrogen at room temperature as is reported in Table 6.

TABLE 6

Carbon Content	Treatment	Time to Start Evaluation Min	Rate of Permeation cm^3/hr
.06	normalized from 1705°F	18	.44
.31	normalized from 1650°F	25	.28
.59	normalized from 1560°F	39	.22

Bardenheur and Thankheiser[23] showed that the microstructure of the carbide also affects the diffusivity. They observed 12 times greater hydrogen permeation rates when the cementite (iron carbide) was in a globular form than when it was in the form of coarse lamellar pearlite.

If the rate of hydrogen flow is determined by the rate of diffusion, than the permeation would be inversely proportional to the thickness of the metal wall. Such a relationship exists from material thicknesses greater than 1 mm thick. For thicknesses less than 1 mm thick, there is a two order magnitude decrease in the diffusion coefficient in going from 1 mm to 0.10 mm of thickness according to Smialowski[26].

Conflicting results have been published concerning the effect of cold work on the diffusivity of hydrogen in steel. This can best be appreciated by the work of Schumann and Erdman-Jestnister[27] who observed that the permeation rate first increases with increasing cold work and passes through a maximum at about 10 to 20 percent cold work. Further cold working then rapidly decreases the permeation rate. At 60 to 90 percent cold work, the permeability was nearly zero. Thus, four markedly different behaviors are reported for the effect of cold work on the permeation of hydrogen through steel. These experiments were done by cathodically charging the steel with hydrogen.

Frank, Lee and Williams[28] determined the diffusion coefficient of hydrogen and deuterium in SAE 1010 steel in the temperature range of 26 to 86°C. The ratio of the diffusion coefficient of hydrogen to that of deuterium was 1.37 ± .02 which is very close to the square root of the ratio of the masses, 1.414. However, the ratio of the permeation rates varied with temperature, reflecting the variation in the ratio of the solubilities of hydrogen and deuterium with temperature. The permeation ratios versus temperature are tabulated in Table 7.

TABLE 7

Temperature	P_H/P_d
86	9.5
80	10.7
79	10.1
60	6.1
52	4.4
50	6.7
42	5.8
34	4.9
26	4.5

Effects of Coating: A coating such as cadmium can more or less make steel impermeable to hydrogen. Cadmium plating is a known barrier hindering the evolution of hydrogen from charged pieces of steel. Chromium and tin have been reported as diffusion barriers. A thin film of oxide also retarded the diffusion of hydrogen while a coating of lacquer had little effect[29]. Rudd and Vetrano[30] investigated hydrogen permeation of types 321 and 430 stainless steel, Hastelloy B, calorized Type 430 stainless steel, glass-coated type 304 stainless steel and three Hastelloy B samples coated with a proprietary material. Their tests were conducted in the range of 550 to 820°C at hydrogen pressures of 1.1, 1.5 and 2.0 atmospheres. The permeabilities of the uncoated specimens were uniformly much greater than those of the surface treated metals. A 3 to 7 mil coating of a glass enamel on 10 mils of surface calorizing was 10 to 100 times more effective as a hydrogen barrier than was 60 to 120 mils of untreated steel.

3.4.1.4. Permeation in Non-Metals

Continuing studies of diffusion in glass have been made including particularly the outgassing of glass surfaces by diffusing out water, and the permeation of helium through glasses.[31,31] Water readily dissolves in silicate glasses where its presence is seen by the IR absorption band around 2.9 microns. Because of the open network structure of these glasses, helium is highly soluble and diffuses readily. Other diffusers in silicate glass are sodium ion and other alkali metal ions, (which diffuse in glass but also move by eletrolysis), fluoride ion which diffuses to and may outgas as HF from glass surfaces from its reaction with available water, and oxygen which is part of the network structure but which can diffuse to and be released as O_2 from glass surfaces under electron bombardment. Hydrogen permeability of glass is also known particularly in fused silica glass, where it is thought to exist as interstitial molecules. The diffusivity of interstial H_2 in fused silica follows classical diffusion theory with activation energy on an Arrhenius plot of 10.4 kcal/mole. Hydrogen also reacts in fused silica to form hydroxyl which gives rise to "anomalous" diffusivity and hydrogen outgassing at higher temperatures (above 700°C).

Hydrogen diffusion in non-metallic compounds is being studied by Verghese and co-workers,[58] who have reported on hydrogen in BeO, Al_2O_3, and SiC. Tritium diffusion was found to be consistent with classical diffusion solutions in BeO and Al_2O_3. Arrhenius plots were given over the temperature range 200°C to 1200°C. Permeation of hydrogen in tube specimens of Al_2O_3 showed a square root dependence of loading gas pressure, indicating that the diffusing species might possibly be the hydrogen atom. No effects of defect structures or radiation damage were seen, but a strong (4-5 order of magnitude) effect of an MgO impurity was seen with Al_2O_3.

Verghese calculated a 5 to 6 fold decrease in tritium permeation for 2 mm thick stainless steel, when covered by a 10 micron film of Al_2O_3, at a temperature of 500°C. He warns that this result could be greatly modified by radiation-induced damage or transmutation-induced impurity levels in a high neutron flux environment.

3.4.1.4.1. Permeation and Diffusion in Glasses

The following summarizes data from several references concerned with the effects of glass composition and structure on permeation rates. Increasing crystalline (ceramic) content reduces permeation.

Helium Diffusion in Glass

Altemose[33] (1961) measured helium permeation rates through 20 types of glass and fused silica. Spherical glass samples were used and equilibrium flow rates were measured by pumping the gas sample continuously through a mass spectrometer. Sensitivity was 10^{-6} cc-torr/s for helium. Permeation rates measured were in the range $5\ 10^{-12}$ to $2\ 10^{-8}$ cc(STP) s^{-1} cm^2(area)mm^{-1} (thickness) cm^{-1}(Hg) (pressure difference), and temperature in the range of room temperature to 600°C.

Diffusion coefficients were obtained for some of the glasses, from the initial transient gas flow rates. For these glasses, a table of values of D and of solubility S are given at various temperatures. For example, the average solubility of Code 7740 glass was 0.0056 cc/cc/atmosphere helium pressure. Values of D obtained are in the range of 10^{-5} to 10^{-8} cm^2 s^{-1}.

Activation energies were obtained from Arrhenius plots and range from 4.8 to 12.4 kcal/mole. Generally, the permeation rates decrease with increasing values of activation energy. Good correlation was found between the activation energy Q and the mole percent M of network formers (SiO_2, B_2O_3, P_2O_5) which were present, so that permeation rates of these glasses may be calculated from their compositions.

These results are discussed in terms of an irregular glass lattice structure as shown by Zachariasen[54] which contains glass forming oxides in a chain-like network with openings large enough for small gas molecules to permeate. Addition of alkali oxides and alkaline earth oxides is pictured as plugging or blocking these openings. The effective size or number of modifier particles are an important factor in determining permeation rates. Altemose[34] made a few measurements of hydrogen permeability in fused silica as follows:

Temperature	Permeability K
200°C	.38 10^{-10}
400°C	5.3
600°C	23.0

Fused silica thus shows a substantial hydrogen permeation at these low values of temperature.

Effect of Alkali Oxides on the Diffusion of Helium in a Simple Borosilicate Glass

In a further study of helium diffusion in glass, Altemose[35] (1973) determined helium permeation in a series of glasses of varying alkali oxide content. The major effect of Na_2O content increasing from 2 to 13% was a systematic decrease in permeation rate and diffusivity, indicating that the Na+ ion is essentially filling space in the glass network. At 7 mole percent alkali oxide, as the alkali ion size is increased from Li+ to Na+ to K+, the changes in diffusivity and in activation energy indicate that the large ion more effectively plugs the network interstices. Ions larger than K+ appear too large to fill the network and consequently spread the network as well.

The Role of Hydroxyl in the Diffusion of Hydrogen in Fused Quartz

R.W. Lee[42] reviewed the diffusion of hydrogen and water in fused silica. The hydroxyl distribution resulting from hydrogen loading was studied by infra red sectioning technique, and deuterium degassing was studied. A model for diffusion of molecular hydrogen in fused silica distinguishes between "metastable" and "stable" hydroxyl. The data on steady-state hydrogen permeation through fused silica has a first-power dependence on hydrogen pressure and suggests that the diffusing species is interstitial H_2. However in non-steady-state hydrogen diffusion and in water vapor reactions, a divergence from simple diffusion theory is found. The diffusing species apparently is different for hydrogen loading than for water vapor loading; however, the introduction or removal of hydroxyl apparently is important for both.

The "stable" OH is regarded by Lee to involve attachment of a proton to a non-bridging oxygen ion which is part of the silicate network. The "stable" hydroxyl is formed during the fused silica manufacturing process; natural fused silica has a low hydroxyl content, synthetic fused silica has a much higher "stable" hydroxyl content. The "metastable" hydroxyl involves groups for which the oxygen ion is not part of the network; the groups are positioned near network modifier ions, and are mobile.

In high-hydroxyl synthetic fused silica, the permanent hydroxyl levels are several orders of magnitude higher than dissolved molecular hydrogen levels. Here diffusion data shows the metastable hydroxyl is relatively insignificant and the net absorbtion of hydrogen agrees with molecular hydrogen solubility

$$S_n = P/D$$

using data for permeability (P) and diffusivity (D) for hydrogen in fused silica gives

$$S_n = 9.4\ 10^{-8} \exp(1.38\ \text{kcal/mole/RT})\ \text{molecules/cm}^3$$

This represents interstitial solubility of molecular hydrogen which shows a first power dependence on the loading hydrogen gas pressure.

Infra red and mass spectrometric data supports the view (above) that the bulk of the hydroxyl content in high-hydroxyl, synthetic fused silica is of the permanent variety. However, metastable hydroxyl in low-hydroxyl natural fused silica can reach a level 10 times that of permanent hydroxyl. Thus large amounts of hydroxyl can be added to or removed from natural fused silica, but not the synthetic variety.

The large amount of "metastable" or mobile hydroxyl in natural fused silica gives rise to "anomalous" outgassing of hydrogen on heating to temperatures in the range 700-1000°C. Hydroxyl reactions also affect measurements of diffusivity and permeability of hydrogen in natural fused silica. Similar effects on outgassing, diffusivity and permeability of water vapor in natural fused silica are discussed by Lee.

3.4.1.4.2. Permeation and Diffusion in Ceramics

The references indicate that the low permeation rates of ceramics make them the materials of choice as barriers for tritium.

Tritium Diffusion in Al_2O_3 and BeO

Tritium diffusion in aluminum and beryllium oxides was studied by Fowler[56] (1977) by recoiling tritium into specimens and measuring the time rate of tritium release during postirradiation heating. Results were consistent with classical diffusion solutions and gave single values for the diffusion activation energy over the temperature range of measurement for single-crystal, sintered, and powdered specimens. The best fit of all data to Arrhenius plots yields the values, which are consistent with previously reported results in the literature:

	Activation Energy Q (kcal/mole)	D_o (cm^2/s)	Temp. Range (°C)
Al_2O_3	31.5	$6.4\ 10^{-5}$	300 - 1000
Lucalox	41.8	39.8	360 - 570
BeO	30.8	$1.3\ 10^{-6}$	300 - 1200

An initial tritium concentration of .1 ppm was produced by irradiation in both the Al_2O_3 and BeO specimens. Diffusion coefficients determined were in the range $D = 10^{-15}$ to 10^{-9} cm^2s^{-1} for bulk specimens and $D = 10^{-12}$ to 10^{-18} cm^2s^{-1} for powder. Temperature ranges were 500°C to 1200°C for bulk specimens and 200°C to 1200°C for powder.

It was shown that radiation damage did not affect the diffusion results. A significant fraction of released tritium was removed when sent through a cold trap. It is believed to represent tritiated water vapor formed at surfaces when tritium exchanges with water already present. Heated specimens thus released a mixture of tritium gas and tritiated water. The effect was shown not to affect the D values obtained and was ignored.

Lucalox is a commerical polycrystalline alumina containing .2% MgO added to increase ductility and grain boundary strength. Microprobe surface scrans showed substantial amounts of MgO within grains and small amounts of Si at grain boundaries. Tritium diffusion is 4 to 5 orders of magnitude higher for the doped alumina than for undoped alumina. This reflects enhanced diffusion within the doped grains.

The form of the diffusing tritium is unknown. Recoil injection initially produces tritium atoms. It has been shown[57] by ion injection and in spectroscopy that appreciable hydroxyl formation occurs in injected regions in alumina and silica. The formation of molecular hydrogen is possible in the present work as the mean free path to a lattice site occupied by a hydrogen atom is shorter than the path to the free surface. The absence of a hydrogen gas effect on tritium release rate indicates the surface formation of molecular hydrogen is not a rate-limiting step. Roberts states that the observation of high diffusion activation energies suggests that hydrogen does react with the substrate and the diffusion species may involve a molecule associated with a defect complex.

The accelerated diffusion of tritium in MgO-doped alumina (Lucalox) compared with that in pure Al_2O_3 appears to indicate an impurity effect on diffusion, since grain-boundary effects can not account for the size of the change in diffusion rate. The existence of this effect would influence the use of aluminum oxide as tritium barriers in fusion reactors.

A tritium diffusion barrier containing Al_2O_3 or BeO might consist of a ceramic layer on a metal substrate. The equilibrium permeation rates through the composite would be controlled by the diffusion coefficients in the composite, the surface tritium concentrations, the tritium partition coefficient at the interface, and possibly by the tritium transport along grain boundaries. A simple expression for the equilibrium tritium permeation rate for a tritium barrier divided by the permeation rate for the substrate alone is obtained if tritium concentration is assumed to be uniform across the interface, zero at the exit face, and grain-boundary effects are neglected. This calculation is carried out for the metals Nb, W, Mo and S.S. For stainless steel coated with alumina at 500 C, the following is obtained:

Temp. °C	Log (R'/R)
300	-6.8
400	-6.2
500	-5.8
600	-5.3
800	-4.8

Substrate thickness .2 cm

Coating thickness .01 mm = 10μ

Thus at moderate temperatures, the 10 micron coating of alumina has a potential for reducing tritium permeation of 2 mm thick stainless steel by 5 to 6 orders of magnitude.

Hydrogen Permeation of Sintered Aluminum Oxide

Roberts[55] (1979) measured hydrogen permeation of high-density high-purity sintered alumina tubes as a function of temperature and pressure using tritium as a tracer. The permeability ϕ at 1250 to 1450°C and hydrogen partial pressure between 2 to 50 kPa is

$$\phi \text{ (H atoms cm cm}^{-2}\text{s}^{-1}\text{kPa}^{-0.43}) = \exp(48.95)\ \exp(-318.2 \text{ kJ(g.atom)}^{-1}(RT)^{-1}$$

Diffusion coefficients and solubility values deduced from the permeation experiments are consistent with earlier measurements. No accelerated permeation due to microstructural defects or changes during the experiments was observed.

Permeation was determined in a heated tube by circulating a hydrogen, tritium and helium gas mixture through the inside and sweeping permeating hydrogen from the outside with helium. The sweep gas was sent through an ion chamber to determine tritium. Permeation rates were obtained from the steady state values at constant temperature. The changing rates which occurred during the approach to equilibrium after temperature changes or initial heating were used to determine diffusion coefficients for hydrogen in alumina.

Dependence of hydrogen permeability rate on the partial pressure of hydrogen within the alumina tube was measured at pressures of 15 to 380 torr. Permeability appears to vary as the .43 power of hydrogen pressure.

Dependence of permeability on temperature was determined in the range 1200 to 1450°C. The values (normalized to 760 torr) follow an Arrhenius plot giving the activation energy 318.2 kJ/g.atom

76 kcal/mole). Diffusion coefficients also followed an Arrhenius plot. The data on permeation and diffusion appears to follow classical behavior. The pressure dependence of permeability suggests atomic rather than molecular transport of hydrogen through alumina. The square root dependence of permeability on pressure is similar to the hydrogen permeability behavior of metals, where the hydrogen dissociates at the metal surface and diffuses as atomic hydrogen. The measured diffusion coefficients agree well with earlier results of single crystals. Thus grain boundaries and small closed pores did not contribute significantly to accelerated permeation of hydrogen in sintered alumina.

Microstructural examination showed no change in crystal structure or grain boundaries to have occurred during the permeation runs. There was a small increase in porosity and some sag of the tubes resulting from creep during heating in the H_2-He environment, indicating that further bloating and grain growth could occur at higher temperatures than 1450°C.

In materials which do not have rapid diffusion paths, the permeability, ϕ , may be expressed as the product of the solubility, S, and the diffusion coefficient, D. The solubility of hydrogen in alumina was calculated from values of permeability and diffusion coefficient obtained here for comparison with earlier determinations. Roberts values ranging from 10^{17} to 10^{18} H atoms per gram Al_2O_3 (for the temperature range of this study) agree reasonably well with other workers results.

Hydrogen Permeation Through Non-Metals (Al_2O_3 and SiC)

This paper by Verghese[58] (1979) reviews the results of Roberts[55] on permeation of hydrogen in alumina and adds some new information on hydrogen permeation through SiC tubes, obtained in the same equipment. The new information on SiC is reviewed here.

The permeability of the SiC tube was measured over the temperature range 1423 to 1723°K. Hydrogen partial pressure varied from 5 kPa to 18 kPa. Permeability values were changed to equivalent values at 101.3 kPa (1 atm) assuming a square root pressure dependency although the actual pressure dependence of hydrogen permeation in SiC has not been established. The best fit to an Arrhenius plot is given by an activation energy 555 kJ/g.atom. Estimates of hydrogen diffusion coefficients and of hydrogen solubility in SiC were also obtained in this work.

The hydrogen permeability values for SiC show more scatter than for Al_2O_3. Also, the diffusivity and solubility values do not show good agreement with earlier results on SiC. These higher values of permeability and of diffusion coefficient can be interpreted in terms of accelerated diffusion through pores or other microstructural defects in the SiC tube material.

3.4.1.5. Permeation in Ceramic Coated Metals

Permeation rates were measured spectrometrically by Turnbull et. al for several gases through a variety of metals and ceramics.[3] High rates (0.06 to 0.2 liter-microns/hr/cm^2/mm) were measured for 304 stainless steel, Inconel, Kovar, nickel and 52 alloy at 200C. In contrast, the ceramics alumina and Fosterite showed permeation rates below the limits of the equipment sensitivity (0.00002 liter-micron/hr/cm^2/mm) at 750 C.

In 1961-68, Eastman,[4] Ernst, Fox,[5] Kessler, Longsderff, Rhoads and Stern,[61] working at RCA, investigated a large number of ceramic materials as possible barriers to the permeation of combustion products into such vacuum devices as thermionic converters and heat pipes. Particular attention was paid to hydrogen permeation. As noted above, Eastman and Fox measured low hydrogen permeation rates for aluminum oxide.

As a consequence of these measurements and the prior work of Turnbull, a concentrated effort was made to produce a high integrity alumina barrier on a metallic substrate. It was desired to operate the devices at 1200-1600C. For temperature reasons, the substrates were refractory metals, notably molybdenum or its alloys. The initial approach was to apply an alumina coating to the substrate. Flame spraying, plasma spraying and cataphoresis were tried with and without subsequent sintering. It was not found to be possible to form a continuous, vacuum tight, alumina layer which was also well bonded to the substrate. Alternative approaches with somewhat greater success were found in chemical vapor deposition of molybdenum on the inside of pre-formed alumina shells and in shrinking green alumina shells onto pre-formed moly parts. However, the CVD proved inadequately vacuum tight, although well bonded, and the shrunk cap structure eventually failed in thermal cycling, indicating inadequate bond strength.

Similar efforts were made by Eastman, Freggens, Harbaugh, and Longsderff,[61] also at RCA in 1968-70, to produce permeation resistant coatings for austenitic stainless steel and super alloy heat pipes for operation in the 500-1000 C range from flame heat sources. It was shown qualitatively that the chrome oxide formed on stainless parts could reduce permeation rates, but that the results were erratic. It was concluded from indirect evidence that the oxide layer served primarily to prevent catalytic decomposition of water vapor (and subsequent permeation by the nascent hydrogen) by the nickel on unoxidized stainless surfaces, rather than as a direct barrier to hydrogen permeation as such. However, the oxide layer was extremely well bonded to the substrate and survived thermal cycling well. These desirable characteristics suggested that barrier layers could be formed from substrate alloy constituents.

In 1973-4, Eastman,[61] at Thermacore, devised a means of protecting stainless steel heat pipe envelopes from internal corrosion by water as the working fluid. The process involved the use of aluminum-bearing steel vessels on the surface of which an aluminum oxide layer was formed by diffusion of the aluminum to the surface and oxidation there. A patent (#4,082,575) on this process was granted. A heat pipe using this approach was operated for more than 35,000 hours, including over 11,000 on/off thermal cycles, without degradation.

In 1975, Eastman, at Thermacore, showed that this same structure had markedly lower hydrogen permeation rates than conventional stainless steels when used as an envelope for a sodium heat pipe operating at 700 C from a flame heat source. The improvement appeared to be by a factor of roughly 200.

Samples of the steel alloy, Armco 18-SR, were supplied by Thermacore to Argonne National Laboratory for hydrogen permeation measurements in August 1976. The measurements were quite favorable, a reduction of permeability by a factor of 150 at 600 C as compared to more conventional ferritic stainless alloys.[6,7]

Similar layers have been formed at Thermacore on Armco 2 SR (1.7% Al) by oxidation in humidified hydrogen. Although this structure has not yet been tested for hydrogen permeation, it does show the water compatibility referred to above. Samples have been supplied to Oak Ridge National Laboratory for permeation testing.

J. T. Bell at ORNL[62] has reported a reduction in permeation rates for 406 stainless steel (3.5% Al) when heated in a tritiated steam environment. It is believed these results derive from formation of a surface Al_2O_3 layer by high temperature diffusion followed by steam oxidation.

It has been shown at Thermacore that the alumina layer has a useful self-healing characteristic. If the coating is accidentally chipped or scratched, it will re-form by further diffusion of aluminum to the surface followed by oxidation in air (or steam).

3.4.2. Optimum Aluminum Content for Austenitic Stainless Steels

In the previous section of this report it was shown that oxide films on iron can markedly reduce the permeation rate of hydrogen through iron. When aluminum is added to steel and is fired in an atmosphere which is oxidizing to the aluminum but is reducing to the iron, the aluminum will diffuse to the surface and form a strong adherent film on the surface. The exact nature of the film is not known but one would expect it to be modified by the other alloying elements in the steel.

Investigations of this phenomenon of forming a diffusion barrier on steels by oxidation has been limited to ferritic alloys. The ferritic alloys are magnetic and the question arises; can aluminum or another element having similar oxidation characteristics be added to the austenitic stainless steels? Also, the question of the oxides' compatibility with liquid lithium must be addressed. (See 3.4.3)

According to Zapffee[63] chromium, Vanadium, titanium, molybdenum, columbium, zirconium, tungsten, tantalum, aluminum, silicon and phosphorus are all ferrite forming elements. A ferrite forming element contracts the gamma loop of the iron-carbon phase diagram. An austenitic forming element is one which expands the gamma loop. The austenitizing elements are carbon, nitrogen, nickel, cobalt, iron, manganese, ruthenium, osmium, rhodium, iridium, platinum and palladium. Of these elements aluminum is a much more powerful stabilizer of ferrite than chromium. When four percent aluminum is added to 406 stainless steel, it completely erases all of the austenite.

Oerteil and Schepers[64] investigated adding small amounts of aluminum to 18-8 stainless steel. They reported that aluminum increased the hot strength of the steel with some reduction in elongation and in area. At 1000°C, they observed the properties in Table 8.

TABLE 8

Al Content (%)	Tensile Strength (psi)	Elongation (percent)	Reduction in Area (percent)
.07	14200	26	50
1.31	15500	18	38

Marsh[65] reports that up to 3.5 percent aluminum is soluble in the face centered cubic structure of austenite at a ratio of 70 iron to 30 nickel.

Aluminum may also be added to the steel, diffused into the surface and then oxidized as has been described. Crosby[66] investigated chemically vapor deposited aluminum on steel using triisobutyl aluminum (TIBA). In the process, TIBA was mixed with isobutylene and argon, vaporized and then thermally reacted on a heated steel specimen. Metallic aluminum up to 2 mils thick was deposited on the specimen. The plating parameters were as follows:

Pressure - 760 mm
Specimen temperature - 260°C
Vaporizing temperature - 200°C
Plating chamber temperature - 175°C
Mixed gases temperature - 175°C
Lime between the vaporizer and the plating chamber temperature - 200°C
TIBA flow rate - 0.83 ml/min
Argon flow rate - 515 ml/min
Isobutylene - 75 ml/min

Recently Banerji[67] discussed a "poor man's" austenitic stainless steel. These alloys are essentially free of nickel and chromium. The alloys are designed to expand the gamma loop with manganese and carbon and to add sufficient aluminum for good hot strength, cold workability and good oxidation resistance. In working these metals, Benerji noted that when the steels are heated in the range of 670 to 870° C, a thin protective surface coating forms which does not spall even after prolonged heating. Also the surface could be anodized to provide a continuous aluminum oxide coating for added oxidation and corrosion resistance.

An alloy of (10.2 Al, 34.4 Mn, 0.76 C, bal Fe) exhibited the following physical properties at room temperature and 650°C. Data for type 304 stainless steel are included for comparison.

	ROOM TEMPERATURE		650°C	
	Al-Mn	Type 304	Al-Mn	Type 304
Yield Stength	55,350 psi	33,350 psi	40,000 psi	12,000 psi
Tensile Strength	109,350 psi	84,650 psi	60,000 psi	40,000 psi
Reduction in Area	72%	76%	32%	53.3%
Elongation	73%	63.3%	34%	38.7%

The alloy was about 15 percent lighter than type 302 stainless and exhibited a remarkable ability to be strengthened via work hardening and strain aging. The data tabulated does not reflect the Al-Mn steels ability to be strengthened from work hardening and strain aging. With a 60 percent reduction in area and by aging at 700° for one hour, the hardness of the Al-Mn steel is a Ra of 80 compared to Ra of 68 for type 302 receiving the same degree of work hardening.

A black emissivity coating can be formed on type 321 stainless steel by firing it in a hydrogen atmosphere in the temperature range of 800 to 1100°C. The black film is adherent and is formed by the preferential oxidation of the titanium in the stainless steel. This film has not been investigated as a potential barrier to the permeation of hydrogen but is similar in nature to that of the aluminum bearing steels.

3.4.3. Compatibility with Liquid Lithium

Both the ferritic and austenitic stainless steels are compatible with lithium up to 580°C in a dynamic system and up to 800°C in a static system.[68] The investigations which established the above facts were conducted on unmodified surfaces, that is, not heat treated to form a preferential oxide on the surface. For this reason it is necessary that the thermodynamic stability of the oxides be considered.[69]

A reaction can occur at a given temperature and pressure only if the Gibbs free energy of reaction is negative. The thermodynamically stable products of reaction are those substances that can form with the greatest decrease in the free energy of the system. Changes in chemical stability with increasing temperature can always be traced to changes in the relative importance of the two terms that determine the Gibbs free energy of the possible reactions. Always $\Delta F = \Delta H - T\Delta S$ where ΔF is the Gibbs free energy of the reaction, ΔH is the heat of the reaction, T is the absolute temperature, and ΔS is the entropy of the reaction. Although the final equilibrium that can be attained among the reacting substances is purely a function of the chemical components present and of temperature and pressure, the path of the reaction and the rate of the reaction depend on a variety of additional variables. Among these variables are particle size, the extent of mixing, rate of diffusion, the pressure or absence of inert gas, and even such physical properties of the solid or liquids concerned as strength, coefficient of thermal expansion and viscosity. For these reasons Gibbs free energy can be a useful guide to predict the stability of materials which have a positive difference in their free energies but if the difference is negative, it is not practical to predict the usefulness of the system without farther analysis.

In the case of liquid lithium in a stainless steel container with an oxide on the surface of the steel it would be undesirable to employ any oxide which does not have a free energy less (that is more negative) than lithium oxide Li_2O. Free energy of many of the useful oxides[70] are plotted in Figures 2 and 3. In these figures, the free energy of Li_2O cuts across the free energy relations for zirconium oxide ZrO_2 at 480°C, for aluminum oxide Al_2O_3 at 360°, and for hafnium oxide HfO_2 at 300°C. Below these temperatures the free energy of Li_2O is less than the mentioned compounds and, therefore, if lithium metal is in contact with these oxides, the oxide will be reduced by the lithium but it would be impossible to predict the rate of attack. Further examination of the figures reveals other oxides which have free energies less than Li_2O. These oxides are magnesium oxide, MgO, beryllium oxide, BeO, thorium oxide, ThO_2, calcium oxide, CaO, and yttrium oxide, Y_2O_3. Of these compounds, BeO and Y_2O_3 have excellent strength and will form adherent oxides on their host metal when the element is used for alloying. Less than two percent of beryllium added to copper or nickel prevents solder or noble metal brazing alloys from wetting the base metal when the solders are melted in a hydrogen atmosphere. The oxides of Th, Mg and Ca are weak and in general do not form tenacious oxides on the parent metal.

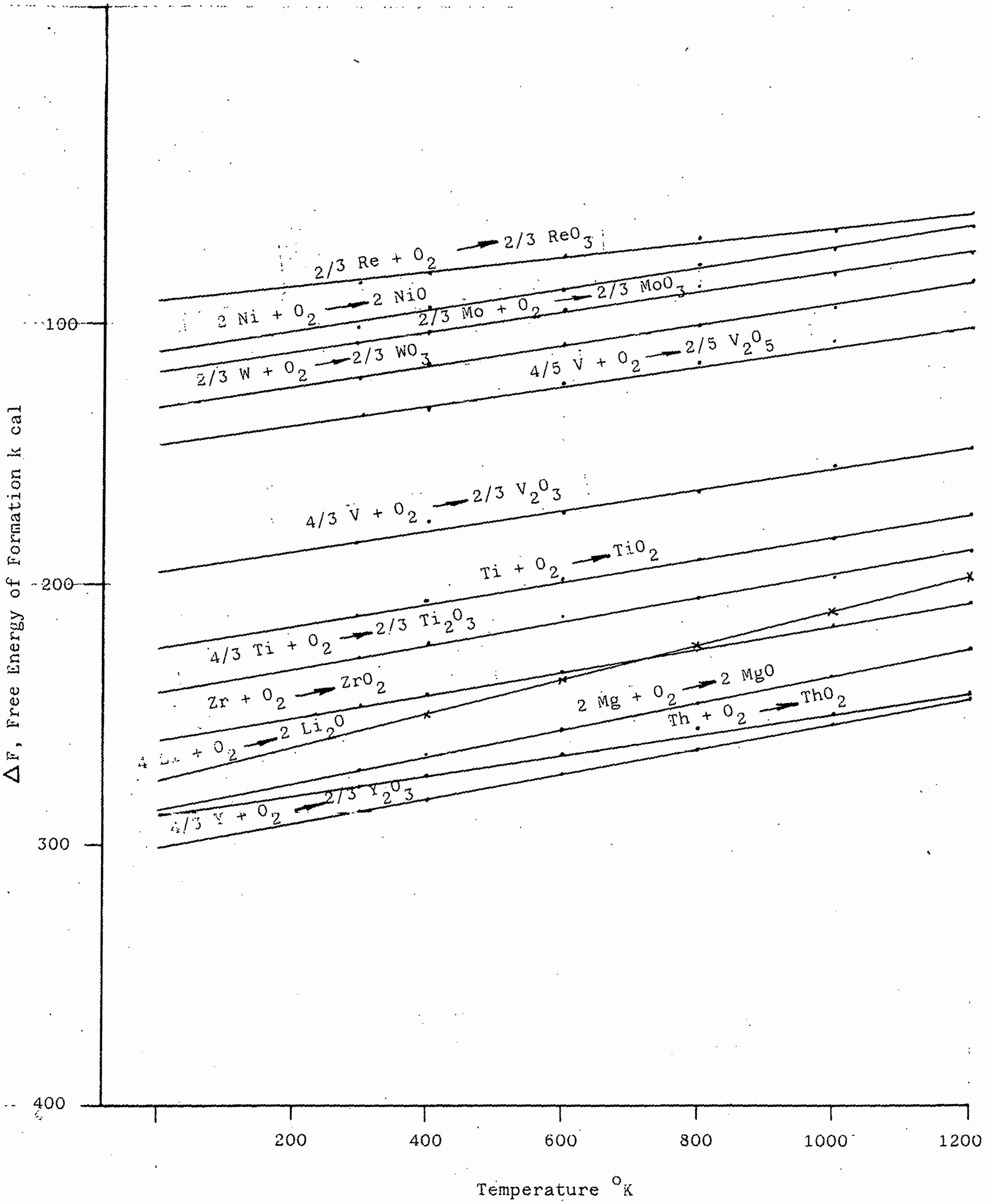

Figure 2

Gibbs Free Energy Diagram I

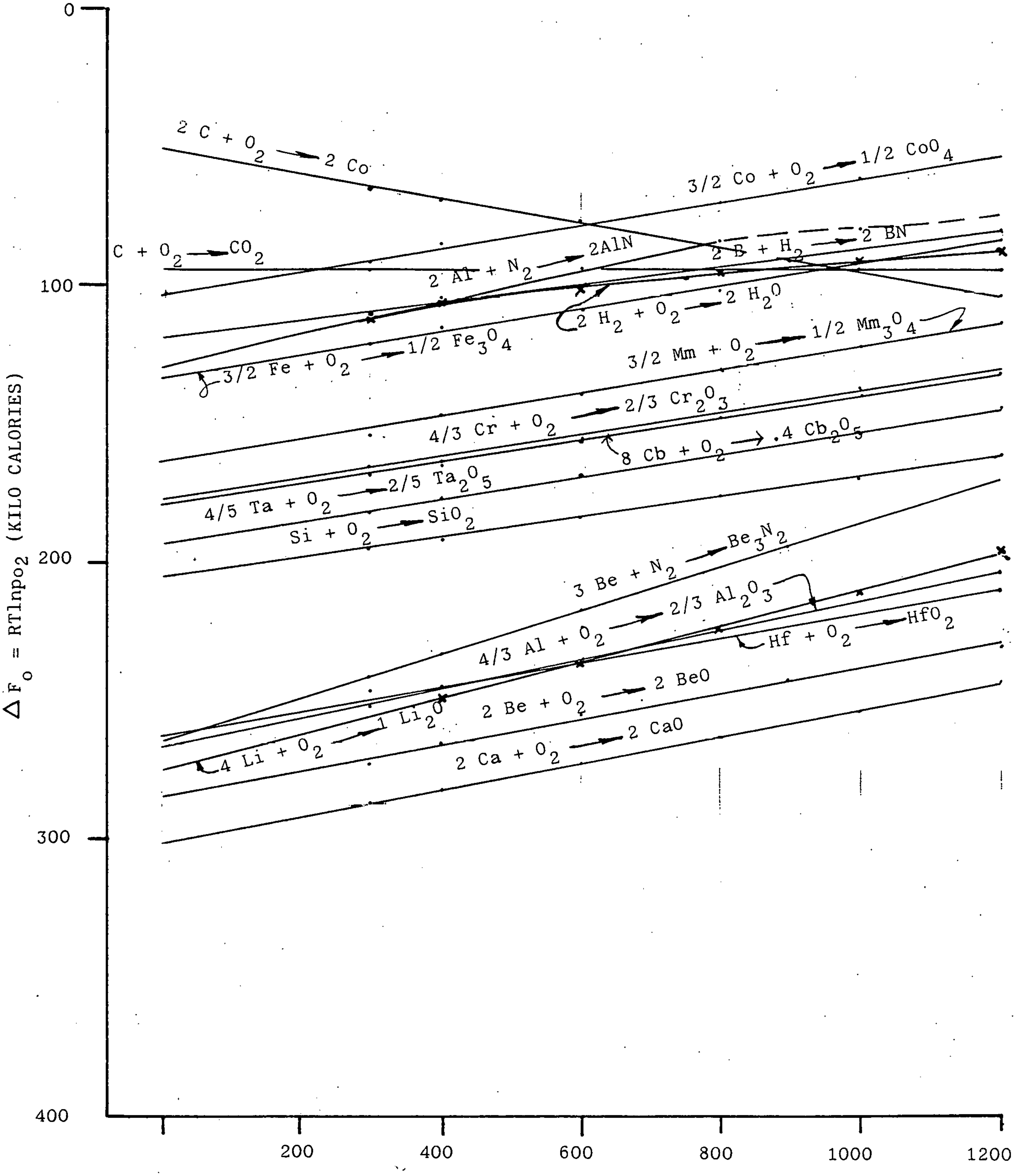

Figure 3

Gibbs Free Energy Diagram II

4. CONCLUSIONS

1. Tritium loss represents a serious potential environmental and personnel hazard in fusion reactors unless suppressed at the source.
2. Tritium loss by permeation can be suppressed in fusion reactor vessels and associated high temperature plumbing.
3. The approach investigated is highly promising for effectiveness, cost and simplicity of fabrication.
4. A thin Al_2O_3 layer can be an effective tritium barrier.
5. An effective suppressive coating can be produced from steels containing .5 to 5% Al.
6. A low cost process has been demonstrated for forming such coatings.
7. The process has been demonstrated to date only on ferritic alloys, but seems feasible on non-magnetic austenitic alloys.
8. High cost non-magnetic alloys (e.g., Inconel 601) may have the desired properties.
9. Lower cost alloys can be developed.
10. The mechanism by which permeation is suppressed is not well understood. It may involve one or all of several factors: inhibition of H_2 dissociation, low solubility and low diffusion constants.
11. Further work is justified in two areas:
    a. Research into the mechanism of hydrogen permeation in these specialty coated alloys.
    b. Development and characterization of improved, non-magnetic alloys having low tritium permeation.

5. RECOMMENDATIONS

The present program represents a minimal investigation of a highly promising method of preventing dangerous levels of tritium permeation from future fusion reactors. The process involves selection or development of a suitable steel alloy containing aluminum as a minor (.5 to 5%) alloying agent. The vessel is formed of this steel. After formation, the vessel is heated in air or humidified hydrogen to diffuse the aluminum to the surface and oxidize it in place. The aluminum layer provides the permeation barrier. It is readily re-formed by reheating if accidentally chipped or otherwise breached.

The process was originally developed to prevent hydrogen permeation into high temperature heat pipes and has been demonstrated only in alloys suitable for that service. There has been no effort to date to tailor alloys for fusion service. The mechanism by which hydrogen permeation is suppressed by these thin (1-2μ) coatings has not been investigated. There is indirect evidence that in addition to reducing hydrogen diffusion, the coatings may also suppress hydrogen dissociation at the surface, thus inhibiting the process at the start. It is recommended that a two-pronged program be initiated with the objective of developing well characterized tritium containment materials for fusion reactors. Such a program might have the following tasks:

Task 1 – Mechanism of Tritium Permeation in Metals with Integral Ceramic Coatings.

REFERENCES CONSULTED

[1] C.J. Smithells and C.E. Ransley, "The Diffusion of Gases Through Metals", Proceedings of the Royal Society, pp. 172-197, 1935.

[2] E. Waldschmidt, "Gas Release and Permeation of Metals Used in the Construction of Vacuum Tubes" Metall, Vol. 5, pp. 749-758, Oct. 1954 (In German).

[3] J.C. Turnbull, et. al., "A Study of High Temperature Microwave Tube Design and Processing", Phase I Report, Contract AF33 (616) - 6563, June 1960.

[4] G.Y. Eastman, "Emitter Shell Materials for Fossil Fuel Heated Thermionic Converters", 18th Power Sources Conference, May, 1964, pp. 143-146.

[5] G.Y. Eastman and J.A. Fox, "Emitter Shell Materials for Fossil Fuel Fired Thermionic Converters", 19th Power Source Conference, May, 1965, pp. 151-154.

[6] V.A. MacLaren, "Characterization of Tritium Permeation Barriers for Fusion Reactors: Computer Studies and Metallographic Analyses" ANL Report, April, 1977.

[7] Tritium Control Technology, A Development of Barriers to Tritium Migration in Fusion Devices and Reactors, April, 1977.

[8] Telephone Communication, 10/4/79, G.Y. Eastman with J. Barblitz, DOE.

[9] Telephone Communication, 10/4/79, G.Y. Eastman with D. Smith, Argonne National Lab.

[10] B. F. Dodge, "High Pressure Research in Chemical Engineering Department of Yale University", Trans. Am. Soc. Mech. Engrs., 75, pp. 331-343 (1953).

[11] G. Borelius and S. Lindblom, "Durchgang von Wosserstaff durch Metalle" (Passage of Hydrogen Through Metals), Ann. Physik 82 Series 4, p. 201-226 (1927).

[12] P. Cotterill, "The Hydrogen Embrittlement of Metals", Progress in Metal Physics, Vol. 9. (Bruce Chalmers, Ed.) Pergamon Press, New York, NY, pp. 201-301 (1961).

[13] P.G. Bastien, "The Phenomena of Cracking and Fracture of Steel in the Presence of Hydrogen". Corrosion Under Stress in the Presence of Moist Hydrogen Sulfide", *Physical Metallurgy of Stress Corrosion Fracture* (Thor N. Rhodin, Ed.), Amer. Inst. Mining, Met., and Petrol. Engrs., Met. Soc. Conf. Vol. 4, Interscience, New York, NY, pp. 311-340 (1959).

[14] P. Bastien, "Phenomena of Fissuring and Cracking of Steel in the Presence of Hydrogen", Arch. Hutnictwa, 4, p. 93 (1959).

[15] M.H. Armbruster, "The Solubility of Hydrogen at Low Pressure in Iron, Nickel, and Certain Steels at 400 to 600° C", J. Am. Chem. Soc. 65, pp. 1043-1054 (1943).

[16] N.J. Hawkins, "Solubility of Hydrogen Isotopes in Nickel and Type 347 Stainless Steel", Report No. KAPL - 868, U.S. Atomic Energy Commission Publication (1953).

[17] M.L. Hill and E.W. Johnson, "Hydrogen in Cold Worked Iron - Carbon Alloys and the Mechanism of Hydrogen Embrittlement", Trans. Met Soc. AIME, 215, pp. 717-725 (1959).

[18] C. Sykes, H.H. Burton and C.C. Gegg, "Hydrogen in Steel Manufacture", J. Iron Steel Inst., 156, pp. 155-180 (1947).

[19] H. Bennek and G. Klotzbach, "Einfluss von Wasserstoffgehalt, Wasserstoffdurchlassigkeit und Wasserstoffloslichkeit and die Flockenbildung inn Stahl", Stahl u. Eisen, 61 (25), 597-606, June 19, 1941; 61 (26), pp. 624-630, June 26, 1941.

[20] W. Geller and T. Sun, "Einfluss von Legierungszusatzen auf die Wasserstoffdiffusion inn Eisen und Beitrag zum System Eisen-Wasserstoff", Arch Eisenhuttenw., 21, pp. 423-430 (1950).

[21] T.M. Stross and F.C. Tompkins, "The Diffusion Coefficient of Hydrogen in Iron", J. Chem. Soc. (London), pp. 230-234 (1956).

[22] E.W. Johnson and M.L. Hill, "The Diffusivity of Hydrogen in Alpha Iron", Trans. Met. Soc. AIME, 218, pp. 1104-1112 (1960).

[23] P. Bardenheuer and G. Thanheise, "Untersuchungen uber das Beizen von kohlenstoffarmen Flusstahlblechen", Mitt. Kaier Wilhelm Inst. für Eisenforschung, 10, pp. 323-342 (1928).

[24] J.D. Hobson, "The Diffusion of Hydrogen in Steel at Temperatures of -78° to 200° C", J. of Iron Steel Inst., 189, pp. 315-321 (1958).

[25] U.V. Bhat and H.K. Lloyd, "Effect of Cold-Work on Hydrogen in Steel", J. Iron Steel Inst., 165, pp. 382-389 (1950).

[26] M. Smialowski, "Hydrogen in Steel" Pergamon Press, Oxford, and Addison Wesley Publishing Co., Inc., Reading, MA, pp. 70-111 (1962).

[27] H. Schumann and F. Erdmann-Jesnitzer, "Einfluss des Werkstoffzustandes auf die Wasserstoffdiffusion in unlegiertem Stahl", Arch Eisenhuttenw., 24, pp. 353-360 (1953).

[28] R.C. Frank, R.W. Lee and R.L. Williams, "Ratio of the Diffusion Coefficients for the Diffusion of Hydrogen and Deuterium in Steel", J.A. Physics, Volume 29, pp. 898-900 (1958).

[29] Morris, T.N., "The Diffusion of Hydrogen Through Mild Steel Sheet During Acid Corrosion", J. Soc. Chem. Ind. (London), 54, pp. 7T-13T (1935).

[30] D.W. Rudd and J.B. Vetrano, "Permeability of Metals and Enamelled Metals to Hydrogen", Report No. NAA-SR-6109 North American Aviation, Inc., Canoga Park, CA, under AEC Contract AT (11-1)-GEN-8 (Oct. 30, 1961).

[31] R.M. Barrer, "Diffusion in and Through Solids, Cambridge Univ. Press, 1941. (Contains References on work up to 1938).

[32] F.J. Norton, "Helium Diffusion Through Glass", J. Am. Cer. Soc., 36,

[33] V.O. Altemose, "Helium Diffusion Through Glass", J. Appl. Phys., 32, 7, 1309, July 1961.

[34] V.O. Altemose, "Gas Permeation Through Glass", Seventh Symp. on Art of Glassblowing, ASGS, 1962.

[35] V.O. Altemose, "Effect of Alkali Oxides on the Diffusion of Helium in a Simple Borosilicate Glass." J. Am. Cer. Soc., 56, 1, 1, (1973) Enclosed.

[36] V.O. Altemose and A.R. Kacyon, "Vacuum Compatibility of Machinable Glass-Ceramics", J. Vac. Sci. & Technol., 16, 3, 951, (1979). Enclosed.

[37] C.C. Leiby and C.L. Chen, "Diffusion Coefficients Solubilities, and Permeabilities of He, Ne, H_2, & N_2 in VYCOR Brand Glass.", J. Appl. Phys., 31, 268, (1960).

[38] D.R. Swets, R.W. Lee, and R.C. Frank, "Diffusion Coefficients of Helium in Fused Quartz", J. Chem. Phys., 34, 1, Jan. (1961).

[39] D.R. Swets, R.W. Lee, and R.C. Frank, "Coefficients of Neon Isotopes in Fused Quartz", J. Chem. Phys., 35, 4, Oct. 1961.

[40] D.R. Swets, R.W. Lee, and R.C. Frank, "Diffusion of Hydrogen and Deuterium in Fused Quartz", J. Chem. Phys., 36, 1062, (1962).

[41] R.W. Lee, "Diffusion of Hydrogen in Natural and Synthetic Fused Quartz", J. Chem. Phys. 38, 2, Jan. 1963.

[42] R.W. Lee, "The Role of Hydroxyl in Diffusion of Hydrogen in Fused Silica", Phys. & Chem. of Glasses, 5, 2, (1964).

[43] R.H. Doremus, "Physical Solubility of Gases in Fused Silica", J. Am. Cer. Soc., 49, 9, 461 (1966).

[44] W.C. Perkins and D.R. Begeal, "Diffusion and Permeation of He, Ne, Ar, Kr, and O_2 through SiO_2 Thin Films", J. Chem. Phys., 54, 4, 1683 (1971).

[45] K.P. Srivastava and G.J. Roberts, "Effect of Thermal History on the Diffusion of He and Ne Through Vitreous Silica", Phys. & Chem. Glasses, 11, 2, April 1970.

[46] R.W. Lee and D.L. Fry, "A Comparative Study of the Diffusion of Hydrogen in Glass", Phys & Chem. Glasses, 7, 1, Feb. 1966.

[47] J.E. Shelby, "Diffusion of Helium Isotopes in Vitreous Silica", Phys. Rev. B, 4, 8, 2681, Oct. 15, (1971).

[48] J.E. Shelby, "Helium Migration in Natural and Synthetic Vitreous Silica", J. Am. Cer., Soc., 55, 2, 61 (1972)

[49] J.E. Shelby, "Effect of Phase Separation on He Migration in Sodium Silicate Glasses", J. Am. Cer. Soc., 56, 5, 263 (1973).

[50] J.E. Shelby, "Helium Diffusion and Solubility in Potassium Silicate Glass", J. Am. Cer. Soc., 57, 6, 260 (1974).

[51] J.E. Shelby, "Effect of Thermal History on Helium Diffusion and Solubility in Vitreous B_2O_3 and Sodium Borate Glass", J. Appl. Phys., 44, (10), 4588 (1973).

[52] C.J. Major and Karl Kammermeyer, "Gas Permeability of Plastics", Modern Plastics, July 1972.

[53] G.M. Kline, "Permeability of Polymers to Gases, Vapors and Liquids", Modern Plastics, March 1966.

[54] W.H. Zachariasen, "Atomic Arrangement in Glass", J. Amer. Chem. Soc., 54 (10) 3841-51 (1932).

[55] Rodney M. Roberts, Thomas S. Elleman, Hayne Palmour III, and Kuruvilla Verghese, "Hydrogen Permeability of Sintered Aluminum Oxide", Jour. Amer. Cer. Soc., 62 (9-10) 495 (1979).

[56] J.D. Fowler, Dipankar Chandra, T.S. Elleman, A.W. Payne, and Kuruvilla Verghese, "Tritium Diffusion in Al_2O_3 and BeO", Jour. Amer. Cer. Soc., 60 (3-4) 155 (1977).

[57] D.M. Gruen, R.B. Wright, R.L. McBeth, and I. Sheft, "Hydroxyl Formation Accompanying Defect Center Production in Proton and Deuteron Bombarded Aluminum Oxide", J. Chem. Phys. 62 (3) 1192-93 (1975).

[58] K. Verghese, L.R. Zumwalt, C.P. Feng, and T.S. Elleman, "Hydrogen Permeation through Non-Metallic Solids", Jour. Nuclear Materials 85 and 86 (1979) 1161-1164.

[59] G. Hetherington, K.H. Jack and M.W. Ramsay, "The high-temperature electrolysis of vitreous silica Part I. Oxidation, ultra-vioulet induced fluorescense, and irradiation colour", Physics and Chemistry of Gasses, 6 (1) 7 (1965).

[60] T. Dunn, G. Hetherington and K.H. Jacks, "The high-termperature electrolysis of vitreous silica Part 2. Active electrodes and anisotropic electrolytes", Phys. and Chem. of Glasses 6 (1) 16 (1965).

[61] Private Files, G. Y. Eastman.

[62] Private Communication, G.Y. Eastman and J.T. Bell, 12/5/79.

[63] Carl A. Fapffe, "Stainless Steel", American Society for Metals, p. 104, (1949).

[64] W. Perteil and A. Schepers, "Hitzebeslandiger Stahl durch Legierung mit Chrom. Nickel-Aluminum und Silizium Stahl u. Eisen, vol. 52, pp. 511-513 (1932).

[65] J.S. Marsh, "The Alloys of Iron and Nickel-Special Purpose Alloys", Vol. 1, pp. 85-87, McGraw Book Co. (1938).

[66] J.J. Crosby, "Vapor Plating of Aluminum on Steel", Tech. Documentary Report No. ASD-TDR-62-907, Dec. 1962.

[67] S.K. Banerji, "An Austenitic Stainless Steel Without Nickel and Chromium", Metal Progress, pp. 59-62, April 1978.

[68] J.H. Stang, E.M. Simons, J.A. DeMastry and J.M. Genco, "Compatibility of Liquid and Vapor Alkali Metals with Construction Materials", DMIC Report, 227, April 15, 1966.

[69] A.W. Searcy, "Chemistry at High Temperatures: The Problem of Reducing Chemical Attack" Chapter 3 of "Modern Ceramics: Some Principles and Concepts", Ed. J.E. Hove and W.C. Riley, John Wiley and Sons, Inc., New York, NY, 1965.

[70] C.E. Wicks and F.E. Block, "Thermodynamic Properties of 65 Elements Their Oxides, Halides, Carbides, and Nitrides", Bulletin 605 Bureau of Mines, United States Department of the Interior (1963).

[71] P.L. Chang and W.D.G. Bennett, "Diffusion of Hydrogen in Iron and Iron Alloys at Elevated Temperatures", J. Iron Steel Inst., 170, pp. 205-213. (1952)