Tritium Barriers and Tritium Diffusion in Fusion Reactors

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Tritium and deuterium induce radiation in reactor materials and some radioactive tritium gas may be released. Most of the materials used in fusion reactors are metals that have relatively high permeabilities for tritium. The fusion community has been working on barriers to minimize tritium release. Unfortunately, most barrier materials work very well during laboratory experiments, but fail to meet requirements when placed in radiation environments.

This chapter presents tritium permeation characteristics of various materials used in fusion reactors, including plasma-facing, structural, and barrier materials. The necessary parameters for tritium release calculations for various regions of a fusion reactor are given.

4.116.1. INTRODUCTION

As fusion energy research progresses over the next several decades, and ignition and energy production are attempted, the fuel for fusion reactors will be a combination of deuterium and tritium. From a safety point of view, these are not the ideal materials. The reaction of deuterium plus tritium produces alpha particles and 14.1 MeV neutrons. These neutrons are used to breed the tritium fuel, but also interact with other materials, making some of them radioactive. While the decay of tritium produces only a low energy beta, tritium is difficult to contain. Additionally, being an isotope of hydrogen, the tritium can become part of the hydrocarbons that compose our bodies.

From the tritium point of view, the fusion facility can be divided into three components: the inner vessel area where the plasma is formed; the blanket where tritium production occurs; and the tritium exhaust and reprocessing system. There is the potential for tritium release to occur in all three sections of the facility. The tritium cycle for a fusion reactor begins in the blanket region. It is here that the tritium is produced by the interaction of neutrons with lithium. Specifically, the reaction is given symbolically as ${}^6\text{Li}(n,\alpha){}^3\text{H}$. A neutron that has been thermalized, or lowered in energy by interaction with surrounding materials, is absorbed by ${}^6\text{Li}$ to produce both an alpha particle (helium nucleus) and a triton. Elemental lithium contains approximately 7.5% ${}^6\text{Li}$. As a breeder material in a fusion plant, lithium is enriched in the ${}^6\text{Li}$ isotope to various degrees, depending on the particular blanket design. The ${}^7\text{Li}$ isotope also produces a small amount of tritium via the ${}^7\text{Li}(n,\alpha){}^3\text{H} + n$ reaction. The cross section for this endothermic reaction is much smaller than that for the ${}^6\text{Li}$ reaction. Upon release from the lithium breeder, the tritium is separated from other elements and other hydrogen isotopes. It is then injected into the torus as a gas or frozen pellet. It then becomes part of the plasma. A fraction of the tritium fuses with deuterium as part of the fusion process, or it is swept out of the chamber by the pumping system. If it is removed from the torus by the pumping system and sent to the reprocessing system, it is again filtered to separate it from other elements and separated from the other isotopes. All through the different steps, there is the potential for the tritium to permeate through the materials containing it, and for it to be released to the environment. The probability of this occurring depends on the location in the tritium cycle. This chapter describes the hydrogen permeability through candidate plasma-facing and structural materials that are anticipated to be used in fusion reactors.

With respect to tritium permeation, fusion reactor materials can be divided into two categories. There are plasma-facing materials and structural materials. The plasma-facing materials in future fusion devices will be heated by the high-energy neutrons, by direct interaction of the plasma particles, and by electromagnetic energy released from the plasma. These plasma-facing materials must be cooled. It is primarily through the cooling tubes passing through the plasma-facing materials that tritium losses can occur in the primary vacuum vessel. The three materials typically used for plasma-facing applications are carbon, tungsten, and beryllium. In this report, we will describe the behavior of these materials as plasma-facing materials and how tritium can be lost to the cooling system.

The term “structural material” is used here to describe materials that serve as the vacuum boundary in the main chamber, as the containment boundary for the blanket region, and as the piping for cooling and vacuum lines. These materials can be ferritic and austenitic steels, vanadium alloys, and zirconium alloys, as well as aluminum alloys in some locations, or

potentially ceramics. We give a complete listing of the different types of structural materials and cover their tritium permeation characteristics.

Materials with a low permeability for tritium are being considered as barriers to prevent the loss of tritium from fusion plants. There are a few metals with relatively small permeability values, but as a whole, metals themselves are not good barriers. Ceramics, on the other hand, are typically very good barriers if they are not porous. In most cases, the low permeation is due to extremely low solubility of hydrogen isotopes in ceramic materials. Bulk ceramics, such as silicon carbide, may one day be used as tritium permeation barriers, but most of the barrier development is presently for oxides, nitrides, or carbides of the metals themselves. We will show in this review that many such oxides and nitrides may exhibit extremely good permeation behavior in the laboratory, but fail miserably when used in a radiation environment. We will review the permeation parameters for all of the materials being considered for barriers.

This report will begin with a review of the processes that control the uptake and transport of hydrogen isotopes through materials. The parameters used to define these processes include diffusivity, solubility, permeability, trapping coefficients, and recombination-rate coefficients. We examine the transport of hydrogen isotopes in plasma-facing materials, discuss the conditions that exist in the main torus, and look at the ways that tritium can be lost there. Next, we consider the tritium transport properties of structural materials, followed by the transport properties in barrier materials, including oxides, nitrides, and carbides of structural metals, as well as low-permeation metals. The application of tritium barriers is discussed in some detail: both the theoretical performance of barriers and their observed performance in radiation environments, as well as an example of tritium permeation in the blanket of a fusion reactor. We finish by summarizing the tritium permeation properties of all the materials, providing the necessary parameters to allow designers of fusion reactors to predict tritium losses during operation.

4.116.2. BACKGROUND

Hydrogen and its isotopes behave similarly in many regards. Gaseous protium, deuterium and tritium are all diatomic gases that dissociate, especially on metal surfaces, and dissolve into the metal lattice in their atomic form (in some materials, such as polymers and some ceramics, the molecules may retain their diatomic character during penetration of the material). The isotope atoms readily recombine on the free surfaces, resulting in permeation of the gaseous hydrogen isotopes through metals that support a gradient in hydrogen concentration from one side to the other. In order to understand this process it is necessary to characterize the source of the hydrogen isotope as well as its transport within the materials.

For the purposes of the following presentation, we will focus on tritium and its transport through materials. Much of the discussion is equally valid for the deuterium and protium as well. In this section we will provide background on the diffusivity and solubility of tritium in metals and relate these thermodynamic parameters to the permeability. In addition, we will discuss the role of trapping of hydrogen isotopes on transport of these isotopes, as well as kinetically-limited transport phenomena such as recombination.

4.116.2.1. *Equation of State of Gases*

In the case of gaseous exposure, the ideal gas equation of state characterizes the thermodynamic state of the gas:

$$V_m^o = RT/p; \quad (1)$$

where V_m^o is the molar volume of the ideal gas, T is the temperature of the system in Kelvin, p is the partial pressure of the gaseous species of interest, and R is the universal gas constant equal to $8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$. The ideal gas equation of state provides a good estimate for most gases, particularly at low pressure (near ambient) and elevated temperature (greater than room temperature). In the context of materials exposed to hydrogen isotopes in fusion technologies, the assumption of ideal gas behavior is a reasonable estimate for gaseous hydrogen and its isotopes. More details about the equation of state for real gaseous hydrogen and its isotopes can be found in Ref. [1].

4.116.2.2. Diffusivity

Tritium diffusion in metals is simply the process of atomic tritium moving or hopping through a crystal lattice. Tritium tends to diffuse relatively rapidly through most materials and its diffusion can be measured at relatively low temperature. The diffusivity, D , is a thermodynamic parameter, therefore, it follows the conventional Arrhenius-type dependence on temperature:

$$D = D_o \exp\left(-E_D/RT\right); \quad (2)$$

where D_o is a constant and E_D is the activation energy of diffusion. Measuring tritium diffusion is non-trivial due to the availability of tritium. Therefore, hydrogen and deuterium are often used as surrogates. From classic rate theory, it is commonly inferred that the ratio of diffusivity of hydrogen isotopes is equivalent to the inverse ratio of the square root of the masses of the isotopes:

$$\frac{D_T}{D_H} = \sqrt{\frac{m_H}{m_T}}; \quad (3)$$

where m is the mass of the respective isotope, and the subscripts T and H refer to tritium and hydrogen respectively. When this approximation is invoked, the activation energy for diffusion is generally assumed to be independent of the mass of the isotope. Diffusion data at subambient temperatures do not support equation 3 for a number of metals [2], however, at elevated temperatures, the inverse square root dependence on mass generally provides a reasonable approximation (especially for fcc structural metals) [3-9]. While equation 3 provides a good engineering estimate of the relative diffusivity of hydrogen and its isotopes, more advanced theories have been applied to explain experimental data; for example, quantum corrections and anharmonic effects can account for experimentally observed differences of diffusivity of isotopes compared to the predictions of equation 3 [3, 10]. For the purposes of this report we assume that equation 3 is a good approximation for the diffusion of hydrogen isotopes (as well as for permeation) unless otherwise noted, and we normalize reported values and relationships of diffusivity (and permeability) to protium.

4.116.2.3. Solubility

The solubility (K) represents equilibrium between the diatomic tritium molecule and tritium atoms in a metal according to the following reaction:

The solubility, like diffusivity, generally follows the classic exponential dependence of thermodynamic parameters:

$$K = K_o \exp\left(\frac{-\Delta H_s}{RT}\right); \quad (5)$$

where K_o is a constant and ΔH_s is the standard enthalpy of dissolution of tritium (also called the heat of solution), which is the enthalpy associated with the reaction expressed in equation 4. A word of caution: the enthalpy of dissolution is sometimes reported per mole of gas (i.e., with regard to the reaction $\text{T}_2 \leftrightarrow 2\text{T}$ as in Ref. [11]), which is twice the value of ΔH_s as defined here. The chemical equilibrium between the diatomic gas and atomic tritium dissolved in a metal (equation 4) is expressed as

$$\frac{1}{2}\left(\mu_{\text{TT}}^o + RT \ln \frac{p_{\text{TT}}}{p_{\text{TT}}^0}\right) = \mu_{\text{T}}^o + RT \ln c_0; \quad (6)$$

assuming a dilute solution of dissolved tritium and ideal gas behavior, where c_0 is the equilibrium concentration of tritium dissolved in the metal lattice in the absence of stress, μ_{TT}^o is the chemical potential of the diatomic gas at a reference partial pressure of p_{TT}^0 , and μ_{T}^o is the chemical potential of tritium in the metal at infinite dilution. This relationship is the theoretical origin of Sievert's Law:

$$c_0 = K(p_{\text{TT}})^{1/2}; \quad (7)$$

where to a first approximation, the solubility is equivalent for all isotopes of hydrogen.

It is important to distinguish between solubility and concentration: the solubility is a thermodynamic property of the material, while the concentration is a dependent variable that depends on system conditions (including whether equilibrium has been attained). For example, once dissolved in a metal lattice, atomic tritium can interact with elastic stress fields: hydrostatic tension dilates the lattice and increases the concentration of tritium that can dissolve in the metal, while hydrostatic compression decreases the concentration. The relationship that describes this effect in the absence of a tritium flux [12-14] is written as

$$c_L = c_0 \exp\left(\frac{V_T \bar{\sigma}}{RT}\right); \quad (8)$$

where c_L is the concentration of tritium in the lattice subjected to a hydrostatic stress ($\bar{\sigma} = \sigma_{ii}/3$), and V_T is the partial molar volume of tritium in the lattice. For steels, the partial molar volume of

hydrogen is approximately $2 \text{ cm}^3 \text{ mol}^{-1}$ [15], which can be assumed to first order to be the same for tritium. For most systems, the increase of tritium concentration will be relatively small for ordinary applied stresses, particularly at elevated temperature; for example, hydrostatic tension near 400 MPa at 673 K results in ~15% increase in concentration. On the other hand, internal stresses near defects or other stress concentrators can substantially increase the local concentration near the defect. It is unlikely that local concentrations will significantly contribute to elevated tritium inventory in the material, but locally elevated concentrations of hydrogen isotopes become sites for initiating and propagating hydrogen-assisted fracture in structural metals.

4.116.2.4. Trapping

Tritium can bond to microstructural features within metals, including vacancies, interfaces, grain boundaries and dislocations. This phenomenon is generally referred to as “trapping” [15-18]. The trapping of hydrogen and its isotopes is a thermally governed process with a characteristic energy generally referred to as the trap binding energy E_t . This characteristic energy represents the reduction in the energy of the hydrogen relative to dissolution in the lattice [16, 19] and can be thought of as the strength of the bond between the hydrogen isotope and the trap site to which it is bound. Oriani [16] assumed dynamic equilibrium between the lattice hydrogen and trapped hydrogen

$$\frac{\theta_T}{1 - \theta_T} = \frac{\theta_L}{1 - \theta_L} \exp\left(\frac{E_t}{RT}\right); \quad (9)$$

where θ_T is the fraction of trapping sites filled with tritium and θ_L is the fraction of available lattice sites filled with tritium. According to equation 9 the fraction of trap sites that are filled depends sensitively on the energy of the trap (E_t) and the lattice concentration of tritium (θ_L). For example, traps in ferritic steels, which are typically characterized by low lattice concentrations and trap energy $< 100 \text{ kJ mol}^{-1}$, tend to be depopulated at high temperature ($> 1000 \text{ K}$). For materials with strong traps and high lattice concentration of tritium, trapping can remain active to very high temperatures, particularly if the trap energy is large ($> 50 \text{ kJ mol}^{-1}$). The coverage of trapping sites for low and high energy traps is shown in Figure 1 for two values of K : one material with relatively low solubility of hydrogen and the other with high solubility.

< figure 1 here >

The absolute amount of trapped tritium, c_T , depends on θ_T and the concentration of trap sites, n_T [15]:

$$c_T = \alpha n_T \theta_T; \quad (10)$$

where α is the number of hydrogen atoms that can occupy the trap site, which we assume is one. If multiple trapping sites exist in the metal, c_T is the sum of trapped tritium from each type of trap. A similar expression can be written for the lattice sites:

$$c_L = \beta n_L \theta_L; \quad (11)$$

where n_L is the concentration of metal atoms and β is the number of lattice sites that hydrogen can occupy per metal atom (which we again assume is one). Substituting equations 10 and 11 into equation 9 and recognizing that $\theta_L \ll 1$, the ratio of trapped tritium to lattice tritium can be expressed as

$$\frac{c_T}{c_L} = \frac{n_T}{\left[c_L + n_L \exp\left(\frac{-E_t}{RT}\right) \right]}. \quad (12)$$

Therefore, the ratio of trapped tritium to dissolved (lattice) tritium will be large if c_L is small and E_t is large. Conversely, the amount of trapped tritium will be relatively low in materials that dissolve large amounts of tritium. The transport and distribution of tritium in metals can be significantly affected by trapping of tritium. Oriani postulated that diffusion follows the same phenomenological form when hydrogen is trapped [16]; however, the lattice diffusivity (D) is reduced and can be replaced by an effective diffusivity, D_{eff} , in Fick's first law. Oriani went on to show that the effective diffusivity is proportional to D and a function of the relative amounts of trapped and lattice hydrogen:

$$D_{eff} = \frac{D}{1 + \frac{c_T}{c_L} (1 - \theta_T)}. \quad (13)$$

If the amount of trapped tritium (c_T) is large relative to the amount of lattice tritium (c_L), the effective diffusivity can be several orders of magnitude less than the lattice diffusivity [20]. Moreover, the effective diffusivity is a function of composition of the hydrogen isotopes, depending on the conditions of the test as well as sensitive to the geometry and microstructure of the test specimen. Thus, the intrinsic diffusivity of the material (D) cannot be measured directly when tritium is being trapped. Equation 13 is the general form of a simplified expression that is commonly used in the literature:

$$D_{eff} = \frac{D}{1 + \frac{n_T}{n_L} \exp\left(\frac{E_t}{RT}\right)}. \quad (14)$$

< figure 2 here >

Equation 14 does not account for the effect of lattice concentration, and is therefore inadequate when the concentration of tritium is relatively large. For materials with high solubilities of tritium (such as austenitic stainless steels), trapping may not affect transport significantly and $D_{eff} \approx D$ as shown in Figure 2. For materials with low solubility and relatively large E_t , the effective diffusivity can be substantially reduced compared to the lattice diffusivity (Figure 2). The wide variation of reported diffusivity of hydrogen in α -iron at low temperature is a classic example of the effect of trapping on hydrogen transport [2, 20]: while the diffusivity of hydrogen at high temperature is consistent between studies, the effective diffusivity measured at low temperature is significantly lower (in some cases by orders of magnitude) compared to the Arrhenius relationship established from measurements at elevated temperature. Moreover, the range of reported values of effective diffusivity demonstrate the sensitivity of the measurements to experimental technique and test conditions. For these reasons, it is important to be critical of

diffusion data that may be affected by trapping and be cautious of extrapolating diffusion data to different experimental conditions and temperatures than the measurements, especially if trapping is not well characterized or the role of trapping is not known.

4.116.2.5. Permeability

Permeability of hydrogen and its isotopes is generally defined as the steady state diffusional transport of atoms through a material that supports a differential pressure of the hydrogen isotope. Assuming steady state, semi-infinite plate, and Fick's first law for diffusion $J = -D(dc/dx)$, we can express the steady state diffusional flux of tritium as

$$J_{\infty} = -D \frac{(c_{x_2} - c_{x_1})}{x_2 - x_1}; \quad (15)$$

where c_x is the concentration at position x within the thickness of the plate. Using chemical equilibrium (equation 7) and assuming that the tritium partial pressure is negligible on one side of the plate of thickness t , the steady state diffusional flux can be expressed as

$$J_{\infty} = \frac{DK}{t} p_{TT}^{1/2}; \quad (16)$$

and the permeability, Φ , is defined as:

$$\Phi \equiv DK. \quad (17)$$

Substituting equations 2 and 5 into equation 17, the permeability can be expressed as a function of temperature in the usual manner:

$$\Phi = K_o D_o \exp \left[-(\Delta H_s + E_D) / RT \right] \quad (18)$$

The permeability is a materials property that characterizes diffusional transport through a bulk material, i.e., it is a relative measure of the transport of tritium when diffusion-limited transport dominates; see Ref. [21] for an extensive discussion of permeation. By definition, the permeability (as well as diffusivity and solubility) of hydrogen isotopes through metals is independent of surface condition, since it is related to diffusion of hydrogen through the material lattice (diffusivity) and the thermodynamic equilibrium between the gas and the metal (solubility).

In practice, experimental measurements are strongly influenced by surface condition, such that the measured transport properties may not reflect diffusion-limited transport. Under some conditions (such as low pressure or due to residual oxygen/moisture in the measurement system), the theoretical proportionality between square root of pressure and hydrogen isotope flux does not describe the transport [21, 22], thus studies that do not verify diffusion-limited transport should be viewed critically.

4.116.2.6. Recombination

As shown above, steady-state permeation of hydrogen through materials is normally governed only by solubility and diffusivity. It has been shown [23] that at low pressures, permeation can also be limited by dissociation at the surface. Due to limited data in the literature on this effect (and questions about whether this condition ever really exists), we will not consider this effect in this chapter. It is also possible for permeation to be limited by the rate at which atoms can recombine back into molecules. With the exception of extremely high temperatures, this recombination is necessary for hydrogen to be released from a material. Wherever the release rate from a surface is limited recombination, the boundary condition at that boundary is given by:

$$k_r = C \left(\frac{8}{mT} \right)^{1/2} \frac{s}{K_o^2} \exp \left(\frac{2\Delta H_s - E_x}{RT} \right); \quad (19)$$

where k_r is the recombination-rate constant and c is the concentration of hydrogen near the surface (for this discussion, we assume that there is no surface roughness). The units for k and c are $\text{m}^4 (\text{s} \cdot \text{mol H}_2)^{-1}$ and $(\text{mol H}_2) \text{ m}^{-3}$, respectively.

There are two specific types of conditions that can lead to the hydrogen release being rate limited by recombination. One case occurs for plasma-facing materials where the recombination rate coefficient is relatively low, and the implantation rate is high. With this condition, the concentration of hydrogen in the very-near plasma-exposed surface will increase to the point where J_r is effectively equal to the implantation rate. It is not exactly equal to the implantation rate because there is permeation away from that surface to the downstream surface. The other condition that can lead the hydrogen release being controlled by recombination is when the rate of ingress at the upstream boundary is very slow. This condition can occur either when the upstream pressure is extremely low or a barrier is placed on the upstream surface, and the downstream surface has a relatively low recombination rate constant. In the extreme case, the release rate at the rear is so slow that the hydrogen concentration becomes uniform throughout the material. The release rate from the downstream surface will be $k_r c^2$, where c now represents the uniform concentration. From $c = K p_{TT}^{1/2}$ and Equation 19, it can be seen the recombination-limited permeation is linearly dependent on pressure, rather than having the square-root of pressure dependence of diffusion-limited permeation.

There are various derivations and definitions of the recombination-rate constant. For the case of intense plasma exposure where extreme near-surface concentrations are generated, Baskes [24] derived the recombination-rate constant with the assumption that the rate was controlled by the process of bulk atoms jumping to the surface, combining with surface atoms, and then desorbing. His expression for the recombination-rate constant is:

$$k_r = C \left(\frac{8}{mT} \right)^{1/2} \frac{s}{K_o^2} \exp \left(\frac{2\Delta H_s - E_x}{RT} \right); \quad (20)$$

where C is a constant, s is the sticking constant which depends on the cleanliness of the material surface, and $E_x = \Delta H_s + E_D > 0$, otherwise $E_x = 0$. The sticking constant can be anywhere from 1 for clean surfaces to 10^{-4} or smaller for oxidized surfaces.

Pick and Sonnenberg [25] solved the recombination-rate constant for the case where the near-surface concentration of hydrogen is small. When this concentration is smaller, the rate atoms

jump to the surface does not play an important role in the recombination rate. This conclusion removes E_x from the exponential. The sticking constant in their model is thermally activated: $s = s_o \exp(-2E_C/RT)$, where s_o is the sticking coefficient and E_C is the activation energy for hydrogen adsorption.

Wampler [26] also studied the case for low near-surface concentration to arrive at an expression for the recombination-rate constant. He assumed equilibrium between hydrogen atoms in surface chemisorption sites and atoms in solution, deriving the recombination-rate constant as:

$$k_r = \frac{n_s \nu}{(\beta n_L)^2} \exp\left(\frac{2\Delta H_s}{RT}\right); \quad (21)$$

where n_s is the area density of surface chemisorption sites, and ν is the jump frequency.

These expressions differ, but also display many similarities. Unfortunately, the surface cleanliness dominates the rate of recombination and these theoretical relationships are only relevant for sputter-cleaned surfaces and very low pressures. As an example, Causey and Baskes [27] showed that the Baskes model [24] predicts fairly accurate results for plasma-driven permeation of deuterium in nickel. Comparison to values in the literature for nickel showed other results to differ by as much as four orders of magnitude and to have significantly different activation energies.

4.116.2.7. Irradiation and Implantation

Irradiation and implantation can affect the transport of hydrogen isotopes in materials. Since these effects can be complex and depend on the conditions of the materials and the environment, it can be difficult to draw broad conclusions from the literature. Nevertheless, changes in apparent transport properties are generally attributed to damage and the creation of hydrogen traps [28-31]. Therefore, the effects of irradiation and implantation will depend sensitively on the characteristics of the traps that are created by these processes. The density of damage is an important consideration: for example, it has been shown that helium bubbles are not effective trapping sites for steels [32], likely because in these experiments the density of helium bubbles was relatively low. The energy of the trap will determine the coverage as a function of temperature (equation 9): generally, the effect of trapping will be stronger at low temperatures, especially in materials with low solubility (Figure 2), which can result in substantial increases in hydrogen isotope inventory compared to hydrogen content predicted from lattice solubility. Additionally, irradiation may increase ionization of hydrogen isotopes, thus enhancing apparent permeation [29]. Reactor environments can defeat permeation barriers, for example by damaging the integrity of oxide layers; this will be discussed at the end of this chapter.

4.116.3. FUSION REACTOR MATERIALS

4.116.3.1. Plasma-Facing Materials

Tritium generated in the fusion-reactor blanket will be fed directly into the plasma in the main vacuum chamber. There, the tritium will be partially consumed, but will also interact with the materials composing the first wall. Materials used to line the first wall will be exposed to energetic tritium and deuterium escaping from the plasma. Particle fluxes in the range of

10^{21} (D+T)m⁻²s⁻¹ will continuously bombard the plasma-facing materials. Materials used for the divertor at the top and/or bottom of the torus will be exposed to lower energy particles with a flux of 10^{23} (D+T)m⁻²s⁻¹ or higher. While the neutral gas pressure of tritium will be relatively low at the outer vacuum wall boundary, some minor permeation losses will occur. In reality, the primary concerns in the plasma-facing areas are tritium inventory and permeation into the coolant through coolant tubes. While future power reactors are likely to have primarily refractory metals such as tungsten, present day devices are still using carbon and beryllium. In this section on plasma-facing materials, we will examine the interaction of tritium with carbon, tungsten, and beryllium.

4.116.3.1.1. Carbon

In many ways carbon is ideal for fusion applications. It is a low Z material with a low vapor pressure and excellent thermal properties. The carbon used in fusion applications comes in two forms, graphite and carbon composites. Graphite is typically made using the Acheson process [33]. Calcined coke is crushed, milled, and then sized. The properties of the graphite are determined by the size and shape of these particles. Coal tar is added to the particles and the batch is heated to approximately 1200 K. This process is repeated several times to increase the density of the compact. The final bake is at temperatures between 2900 and 3300 K and takes approximately fifteen days. The final product is quite porous, with a density of around 1.8 to 1.9 g cm⁻³ (compared to a theoretical density of 2.3 g cm⁻³). Graphite is composed of grains (from the original coke particles) with a size of 5 to 50 μm, which are further composed of graphite crystallites with a typical size of 5 nm. Carbon composites are made by pyrolyzing a composite of carbon fibers in an organic matrix. These fibers have a high strength-to-weight ratio and are composed of almost pure carbon. As with graphite, carbon composites are quite porous with a density of less than 2 g cm⁻³. Carbon (as either graphite or carbon composite) will not serve as a vacuum or coolant boundary. Therefore, permeation through the carbon will not directly affect tritium release into the environment. Coolant tubes inside the graphite will control the tritium release to the coolant system. The ways in which hydrogen isotopes can interact with carbon are explored in the following sections.

It is difficult to consider hydrogen isotope permeation in graphite in the same manner as one would for the metals. As was shown by Kiyoshi, *et al.* [34], hydrogen passes rather readily through graphite in the molecular form. It is when one considers the uptake or retention of atomic hydrogen in graphite or a carbon composite that it becomes more interesting. Most graphites have a BET or specific surface area of 0.25 to 1.0 m²g⁻¹ [35]. This presents a lot of surface area for the absorption of hydrogen isotopes. Barrer [36], Thomas [37], and Bansal [38] are only a few of the many that have reported hydrogen retention on carbon surfaces. Activation energies varying from 24 kJ mol⁻¹ to 210 kJ mol⁻¹ have been reported. Once absorbed on a carbon surface, the hydrogen can migrate by jumping from one chemically active site to another. This process occurs for carbon at lower temperatures in a fusion reactor where the plasma provides ionic and atomic hydrogen for direct absorption. Molecular hydrogen can dissociate on carbon surfaces, but only at elevated temperatures (>1000 K). As a plasma-facing material, graphite will be exposed to atomic tritium and deuterium, and these hydrogen isotopes will migrate inward along the open porosity. Several research groups have measured the diffusion coefficient for hydrogen on carbon surfaces. Robell, *et al.* [39] inferred an activation energy of 164 kJ mol⁻¹ for the diffusion during measurements on the uptake of hydrogen on platinized carbon between 573 and 665 K. Olander and Balooch [40] used similar experiments to determine

the diffusion coefficient for hydrogen on both the basal and prism plane: $6 \times 10^{-9} \exp(-7,790/T) \text{ m}^2 \text{ s}^{-1}$ for the basal plane and $6 \times 10^{-11} \exp(-4,420/T) \text{ m}^2 \text{ s}^{-1}$ for the prism plane. Causey, *et al.* [41] used tritium profiles in POCO AXF-5Q graphite exposed to a tritium plasma to extract a diffusivity for tritium on carbon pores of $1.2 \times 10^{-4} \exp(-11,670/T) \text{ m}^2 \text{ s}^{-1}$. An example of the deep penetration of hydrogen isotopes into the porosity of graphite was reported by Penzhorn, *et al.* [42]. Graphite and carbon composite tiles removed from the JET fusion reactor were mechanically sectioned. The sections were then oxidized, and tritiated water was collected for liquid scintillation counting. Relatively high concentrations of tritium were detected tens of millimeters deep into the tiles.

< figure 3 here>

The diffusion or migration of hydrogen isotopes on carbon surfaces occurs at lower temperatures. The solubility, diffusion, and trapping of hydrogen in the carbon grains are higher temperature processes than adsorption and surface diffusion. At higher temperatures ($>1000 \text{ K}$), hydrogen molecules can dissociate and be absorbed at chemically active sites on carbon surfaces. Some of these sites are located on the outside of the grains, but many exist along the edges of the microcrystallites that make up the larger grains. Hydrogen isotopes dissociating on the outer grain surface are able to migrate along the microcrystallite edges, entering into the interior of the grain. It is the jumping from one moderate energy site ($\sim 240 \text{ kJ mol}^{-1}$) to another that determines the effective diffusion coefficient covered next. It is the highest energy sites ($\sim 415 \text{ kJ mol}^{-1}$) on the crystallite surfaces that are called traps (also covered later). Atsumi, *et al.* [43] used the pressure change in a constant volume to determine the solubility of deuterium in ISO 88 graphite. Over the temperature range 1123 and 1323 K, they determined the solubility to be given by $K = 18.9 \exp(+2,320/T) \text{ mol H}_2(\text{m}^{-3} \cdot \text{MPa}^{-1/2})$. This solubility is shown in Figure 3 along with two data points by Causey [44] at 1273 and 1473 K. A negative heat of solution is seen in both sets of data, suggesting the formation of a bond between hydrogen and carbon.

< figure 4 here>

The variation in the diffusivities of hydrogen in graphite determined by various researchers is extreme. This variation results primarily from differences in interpretation of where the diffusion is occurring. A representative assortment of values for the diffusion is shown in Figure 4. Rohrig, *et al.* [45] determined their diffusion coefficient using the release rate of tritium from nuclear grade graphite during isothermal anneals. They correctly used the grain size as the real diffusion distance. The expression for their diffusion coefficient is $D = 4 \times 10^{-6} \exp(-32,510/T) \text{ m}^2 \text{ s}^{-1}$. Causey, *et al.* [46] measured the release rate of tritium recoil injected into pyrolytic carbon to determine the diffusivity. Data from the isothermal anneals resulted in the diffusivity of $D = 3.33 \times 10^{-2} \exp(-49,800/T) \text{ m}^2 \text{ s}^{-1}$. Malka, *et al.* [47] used the release rate of lithium bred tritium in a nuclear graphite to determine the diffusion coefficient $D = 0.83 \exp(-44,070/T) \text{ m}^2 \text{ s}^{-1}$. Atsumi, *et al.* [43] used the desorption rate of deuterium gas from graphite samples that had been exposed to gas at elevated temperatures to determine a diffusivity. Their expression is $D = 1.69 \times 10^{-4} \exp(-30,100/T) \text{ m}^2 \text{ s}^{-1}$. Building on the work of others, Causey [44] proposed an alternative expression for the diffusivity that he labeled “best estimate”. The result was based on uptake experiments for tritium into POCO AFX-5Q graphite, and the assumption that the total uptake is determined by the product of the diffusivity times the solubility. The uptake data were analyzed assuming the expression given by Atsumi, *et al.* [43] for the solubility was correct. His expression for the diffusivity was $D = 9.3 \times 10^{-5} \exp(-32,510/T) \text{ m}^2 \text{ s}^{-1}$. The expression “best

estimate” was used because it properly took into consideration that the grain size was the effective diffusion distance, and that diffusivity was more properly determined by uptake than release. Release rates are strongly affected by trapping.

The trapping of hydrogen isotopes at natural and radiation-induced traps has been examined by several research groups [41, 48-50]. Causey, *et al.* [41] exposed POCO-AFX-5Q graphite to a deuterium-tritium mixture at elevated temperatures in an examination of the kinetics of hydrogen uptake. For temperatures above 1500 K, it was discovered that increasing the pressure did not increase the retention. It appeared that the solubility hit an upper limit at 17 appm. Analysis of the data revealed that the 17 appm did not represent solubility, but a trap density. The trap was determined to have an energy of 415 kJ mol^{-1} . Atsumi, *et al.* [48] found that radiation damage increased the apparent solubility of deuterium in graphite by a factor of 20 to 50 with saturation at a radiation damage level of 0.3 dpa. A significant decrease in the apparent diffusivity was also noted. In a later report, Atsumi, *et al.* [49] determined graphites and composites to vary significantly in their natural retention values. They saw that the saturation retention was inversely proportional to the lattice constant (crystallite size). Radiation damage was seen to decrease the apparent lattice constant and increase the saturation retention. 6 MeV C^+ ions were used by Wampler, *et al.* [50] to simulate neutron damage to different graphites. The trap density increased with damage levels up to 0.04 dpa where the saturation retention was 650 appm. In a defining set of experiments, Causey, *et al.* [28] examined tritium uptake in unirradiated and radiated pitch-based carbon composites. Pitch-based carbon composites have a large lattice parameter due to the sheet-like configuration of the fibers. These composites retained significantly less tritium before and after irradiation than other carbon materials. The conclusion that one should draw is that high-energy trapping occurs at the edge of the hexagonal crystals on the prism plane.

Hydrogen isotope permeation in the normal sense does not apply to graphite and carbon composites. There is inward migration of atomic hydrogen isotopes along porosity at lower temperatures. To calculate the potential tritium inventory for this process, one can put an upper bound by assuming monolayer coverage of the pore surfaces. Typical nuclear grade graphite has a specific surface area of $1 \text{ m}^2 \text{ g}^{-1}$. Complete loading of that amount of surface area yields $2 \times 10^{25} \text{ Tm}^{-3}$, or about 2 g for a 20 m^2 carbon wall that is 10 mm thick. At higher temperatures, molecular hydrogen isotopes, which are moving through the graphite pore system, are able to dissociate and enter the multi-micron sized graphite grains. This migration into the grains occurs along the edges of the nanometer scale microcrystallites. As the hydrogen migrates inward, it decorates high-energy trap sites. The density of these trap sites is higher than the effective solubility derived from the migration rate. Permeation into graphite will not lead to tritium release from a fusion device, but will affect tritium inventory. If one assumes that radiation damage from neutrons has increased the 415 kJ mol^{-1} traps in graphite up to 1000 appm, and that tritium is occupying 100% of those traps, the same 20 m^2 wall 10 mm thick listed above would now contain an additional 100 g of tritium. Occupation of all of the traps is difficult. At lower temperatures, kinetics makes it impossible to achieve the loading. At substantially higher temperatures, the traps do not remain filled.

There is another process called carbon codeposition that can strongly affect tritium inventory in a fusion device. In the codeposition process, carbon eroded from walls of the tokamak is redeposited in cooler areas along with deuterium and tritium from the plasma. Because carbon

codeposition is not a diffusion or permeation process, it will not be covered in this review. The interested reader is referred to a review of this process by Jacob [51].

4.116.3.1.2. Tungsten

Tungsten is another of the plasma-facing materials. Like carbon, it will not be a vacuum barrier. Thus, permeation through the tungsten will not lead to tritium release directly into the environment. It can lead to tritium permeation into the coolant through the coolant tubes inside the tungsten facing materials. Permeation will also affect the tritium inventory of the fusion device. Tungsten has excellent thermal properties with a very high melting point of 3683 K. The problem that tungsten presents to the tokamak designer is the deleterious radiation losses if present in the plasma. Fortunately, the energy threshold for sputtering by hydrogen ions is quite high, 700 eV for tritium [52]. For that reason, tungsten will be used primarily in the divertor region where the energy of the impacting particles can be limited.

< figure 5 here>

There are a limited number of reports on the diffusivity of hydrogen isotopes in tungsten. Frauenfelder [53] measured the rate of hydrogen outgassing from saturated rolled sheet samples at temperatures over the wide temperature range of 1200 to 2400 K. His material was 99.95% pure tungsten. His expression for the diffusivity is $D = 4.1 \times 10^{-7} \exp(-4,527/T) \text{ m}^2\text{s}^{-1}$. Zakharov, *et al.* [54] used 99.99% pure tungsten samples in their permeation techniques to determine the hydrogen diffusivity over the limited temperature range of 900 to 1060 K. Their reported value for the diffusivity is $D = 6 \times 10^{-4} \exp(-12,400/T) \text{ m}^2\text{s}^{-1}$. In the Benamati, *et al.* [55] experiments using tungsten containing 5% rhenium, a gaseous permeation technique was also used. These experiments were performed over the very limited temperature range of 850 to 885 K. Reported diffusivities are shown in Figure 5. There are a couple of reasons why the diffusion coefficient reported by Frauenfelder [53] is widely accepted as most correct. The first of these reasons is the wide temperature range over which experiments were performed. The second reason is that the experiments were performed at a temperature above that where trapping typically occurs. It can be seen in Figure 5 that Zakharov's [54] diffusivity agrees quite well with Frauenfelder's at the highest temperatures, but falls below his values at lower temperatures, where trapping would occur.

< figure 6 here>

The database on hydrogen solubility in tungsten is very limited. The results of the two experimental studies are shown in Figure 6. In the same experiments used to determine the diffusivity, Frauenfelder [53] also measured solubility. Over the temperature range 1100 to 2400 K, samples were saturated at fixed pressures and then heated to drive out all of the hydrogen. Frauenfelder's expression for the solubility is given as $K = 1.49 \times 10^3 \exp(-12,000/T) \text{ mol H}_2(\text{m}^{-3}\text{MPa}^{-1/2})$. Over the more limited temperature range of 1900 to 2400 K, Mazayev, *et al.* [56] also examined hydrogen solubility in tungsten. The agreement with the Frauenfelder's [53] data is quite good in magnitude, but not good in apparent activation energy. As with his diffusivity, the solubility reported by Frauenfelder is typically the value used in predicting the migration of hydrogen in tungsten.

Hydrogen trapping in tungsten has been studied by several research groups. van Veen, *et al.* [57] used bombardment by 2 keV protons in their study of the bonding of hydrogen to voids in single crystal tungsten. Thermal desorption from the samples with appms of voids revealed a broad release peak at 600 to 700 K. It was stated that the release could be modeled as gas going back into solution from the voids with an activation energy of 96.5 to 135 kJ mol⁻¹ controlling the process. Eleveld and van Veen [58], in a similar study, used a lower fluence of 30 keV D⁺ ions in desorption experiments. In these samples containing vacancies but no voids, the release occurred at 500 to 550 K. The authors reported a value of 138 kJ mol⁻¹ for the dissociation enthalpy of deuterium for vacancy type defects. Pisarev, *et al.* [59] used lower fluences of 7.5 keV deuterons into 99.94% pure tungsten samples. During thermal desorption ramps, peaks in the release rates were seen at 350, 480, 600, and 750 K. The release at the highest temperature was only seen in the highest fluences. Garcia-Rosales, *et al.* [60] used 100 eV deuterium implantation to study the trapping and release rate of hydrogen isotopes from wrought and plasma-sprayed tungsten. Two broad desorption peaks at 475-612 K and 670-850 K were seen in the thermal desorption spectra. Modeling of the release data suggested the lower temperature peak to be controlled by both diffusion and trapping at an 82 kJ mol⁻¹ trap. The second release peak was reported to correspond to trapping at defects with an activation energy of 135 kJ mol⁻¹. In experiments with 99.99% pure tungsten and tungsten with 1% lanthanum oxide, Causey, *et al.* [61] examined tritium retention in plasma exposed samples. Modeling of the results suggested two traps, one at 135 kJ mol⁻¹ and another at 241 kJ mol⁻¹. The density of the trapped tritium averaged 400 to 500 appm. Anderl, *et al.* [62] used deuterium implantation into polycrystalline tungsten to determine the correlation between dislocation density on cell walls and deuterium trapping. Annealing tungsten at 1673 K reduced the dislocation density by a factor of seven, subsequently reducing the deuterium trapping by a similar factor. The energy of these traps was estimated to be 125 to 145 kJ mol⁻¹. Unannealed 99.95% pure tungsten was used by Sze, *et al.* [63] in experiments with intense deuterium plasma exposure. Exposure at 400 K resulted in blisters with diameters of 10s of μms. Elevating the temperature to 1250 K eliminated the blisters. Venhaus, *et al.* [64] used high purity foils in experiments to examine the effect of annealing temperature on blistering by deuterium plasma exposure. An unannealed sample and one annealed at 1473 K both exhibited blisters after the plasma exposure. The sample annealed at 1273 K did not blister. There have been a multitude of other reports on blister formation on tungsten samples exposed to various forms of hydrogen implantation [65-68].

< figure 7 here >

High purity 99.95% tungsten was used by Anderl, *et al.* [62] in 3 keV D₃⁺ ion implantation to determine the recombination-rate constant. Over the temperature range of 690 to 825 K, the recombination rate coefficient was given as $k_r = 3.85 \times 10^9 \exp(-13,500/T) \text{ m}^4 (\text{s} \cdot \text{mol H}_2)^{-1}$. This expression is shown in Figure 7 where it is plotted along with the expression given by the Baskes model [24]. It can be seen that there is very little correlation between the measured value and the calculated value. This is not unusual. Impurities on the surface, especially oxide layers, can have a very strong effect on this coefficient.

While tungsten has excellent low permeability for gaseous tritium, it will only be used in fusion devices as a plasma-facing material. As a plasma-facing material, tungsten will be exposed to intense fluxes of energetic tritium and deuterium. With traps for hydrogen at 135 and 241 kJ mol⁻¹ [57-62] at natural and radiation induced defects, it would appear that a substantial tritium inventory could be generated in divertor tungsten. There are several reasons why this

high inventory is not likely to occur. The first reason is the high recombination rate coefficient given above. For recombination-rate constant of $10^{-1} \text{ m}^4 (\text{s} \cdot \text{mol H}_2)^{-1}$ or higher (see Figure 7), the recombination rate on the surface is so rapid as to generate the equivalent of $c = 0$ at the boundary. With the very limited penetration distance of energetic hydrogen in the dense tungsten, most of the implanted material is immediately released back out of the surface. There are also recent reports suggesting that ruptured blisters and very fine cracks near the surface [69-71] will even further reduce the inward migration of deuterium and tritium into the tungsten.

4.116.3.1.3. Beryllium

Beryllium is a low Z material with good thermal characteristics. Additionally, it is a good getter for oxygen impurities in the plasma. The low Z minimizes the radiation losses from the plasma, and the oxygen removal keeps the plasma clean. For these reasons, beryllium has been used in the JET fusion reactor and will be the first wall material for the ITER reactor. Beryllium has interesting hydrogen retention behavior. Beryllium may also be used in the blanket area of future fusion devices as a neutron multiplier to increase the tritium breeding ratio.

< figure 8 here >

Abramov, *et al.* used two grades of beryllium in their permeation-diffusion experiments. These were high purity (99%) and extra grade (99.8%). Adding to the validity of their experimental result was the fact the authors used multilayer permeation theory analysis to take permeation through the outer oxide layer into consideration. For the high grade (99%) beryllium, the diffusivity $D = 8.0 \times 10^{-9} \exp(-4,180/T) \text{ m}^2 \text{ s}^{-1}$ was determined. For the extra grade (99.8%) beryllium, $D = 6.7 \times 10^{-9} \exp(-3,370/T) \text{ m}^2 \text{ s}^{-1}$ was reported for the diffusivity. For a lower purity material (98%), Tazhibaeva, *et al.* [72] also used the multilayer permeation analysis to determine a diffusivity. Over the temperature range of 673-873 K, their reported diffusivity was $D = 9 \times 10^{-12} \exp(-1,745/T) \text{ m}^2 \text{ s}^{-1}$. For the temperature range of 673 to 1173, Jones and Gibson [73] studied tritium diffusivity and solubility for arc-cast beryllium. Beryllium was exposed to tritium gas for various temperatures, times, and pressures during isothermal anneals. After removing the samples to another experimental system, the samples were heated to various temperatures. For the initial heating, the tritium release would rise, but soon fall to zero. Elevating the temperature to a higher temperature would reestablish the tritium release, but again the release would fall. While this behavior is not typical of diffusion controlled release, the data was analyzed to extract an effective diffusivity. They reported the diffusivity to be $D = 3 \times 10^{-11} \exp(-2,200/T) \text{ m}^2 \text{ s}^{-1}$. The different reported diffusivities are shown in Figure 8. It can be seen that the diffusivity reported by Abramov, *et al.* [74] is considerably larger than those of Tazhibaeva, *et al.* [72] and Jones and Gibson [73]. It is apparent that the purity of the beryllium played a strong role in determining the effective diffusivity. Oxygen, the primary impurity in beryllium provides a strong trap for hydrogen. Thompson and Macaulay-Newcombe [75, 76], examined the diffusion of deuterium in single crystal and polycrystalline beryllium. The effective diffusivity in the single crystal material was lower than that for the polycrystalline material. The polycrystalline results agreed quite well with the results reported by Abramov, *et al.* [74]. They suggested the lower diffusivity seen for the single crystal samples was the true diffusivity for beryllium, and that the polycrystalline results represented diffusion along grain boundaries. If hydrogen isotopes migrate along grain boundaries, it is logical that the rate of migration would be affected by oxygen segregated to those boundaries.

< figure 9 here >

The very limited results for hydrogen isotope solubility in beryllium are shown in Figure 9. In the earlier described experiments by Jones and Gibson [73], the solubility was seen to be effectively independent of temperature. From 550 to 1250 K, the tritium solubility was a fixed $2.1 \text{ mol H}_2(\text{m}^{-3}\text{MPa}^{-1/2})$. For sintered, distilled alpha beryllium, Shapovalov and Dukel'skii [77] reported a solubility of $K = 18.9 \exp(-2,020/T) \text{ mol H}_2(\text{m}^{-3}\text{MPa}^{-1/2})$ for the temperature range 673-1473 K. In experiments using 98.5% and 99.8% pure beryllium samples, Swansiger [78] used gaseous uptake of tritium to determine the solubility. The amount of tritium uptake did not increase with increasing sample size. The solubility for the two purity materials was also seen to be the same. Over the temperature range 713 to 783 K, the apparent solubility was given by the expression $K = 5.9 \times 10^6 \exp(-11,620/T) \text{ mol H}_2(\text{m}^{-3}\text{MPa}^{-1/2})$. For temperatures below 650 K, the apparent solubility was seen to rise again. This strange effect was attributed to trapping. It is interesting to note the fact that the apparent solubilities over the temperatures where the three research groups [73, 77, 78] performed their experiments varied by less than one order of magnitude even though the activation energies varied by 96 kJ mol^{-1} . It should be questioned whether the reported values really represent the solubility of hydrogen isotopes in bulk beryllium.

For all plasma-facing materials, there is concern that implantation of energetic deuterium and tritium could lead to excessive retention and permeation. Implantation of hydrogen isotopes into a material with a low recombination-rate constant can lead to a majority of the material being pushed into the bulk of the material. In the limiting case of slow the recombination, 50% of the hydrogen exits the front face and 50% exits the rear face. Langley [79] implanted 25 keV deuterium into 99.1% pure hot isostatic pressed beryllium. The retention was seen to be 100% until the particle fluence reached $2 \times 10^{22} \text{ D m}^{-2}$. The retention flattened to a limit of approximately $2.8 \times 10^{22} \text{ D m}^{-2}$. Wampler [80] recorded similar results for his implantation of 0.5 and 1.5 keV deuterium into 99.6% pure beryllium samples. Saturation occurred at 0.31 D/Be in the implant zone. Yoshida, *et al.* [81] used 99% pure beryllium in his implantation experiments with 8 keV deuterons. Transmission electron microscopy revealed bubble formation at all temperatures between room temperature and 873 K. The bubbles were not removed even by annealing at temperatures up to 973 K. Plasma exposure was used by Causey, *et al.* [82] and by Doerner, *et al.* [83] in low-energy, high-fluence deuterium exposures to beryllium. In both studies, the fractional retention was extremely low and decreased with increasing temperature. Open porosity in the implant zone was listed as the likely cause of the low retention. Chernikov, *et al.* [84] and Alimov, *et al.* [85] showed bubbles and microchannels to be responsible for the behavior of implanted hydrogen in beryllium. At 300 K, very small bubbles with a high volume density are formed even at low fluences. As the fluence is increased, the bubbles agglomerate into larger bubbles and then form microchannels that eventually intersect with the surface. For irradiation at 500 to 700 K, small faceted bubbles and large oblate, gas-filled, cavities are formed. This microstructure was seen to extend well beyond the implant zone. Alimov, *et al.* [85] postulated the hydrogen retention in the porous region was due to binding to the beryllium oxide that forms on the pore surfaces.

Beryllium is known as a neutron multiplier due to the reaction $\text{Be}^9 + n \Rightarrow \text{Be}^8 + 2n$. Another neutron reaction for beryllium is $\text{Be}^9 + n \Rightarrow \text{He}^4 + \text{He}^6$, followed by He^6 decaying to Li^6 . Li^6 has a very large cross section to absorb a thermal neutron and produce a helium atom and a tritium atom. Baldwin and Billone [86] calculated the amount of tritium that could be produced in a

large fusion device of the future. In an experiment, they exposed beryllium to a neutron fluence of $5 \times 10^{26} \text{ n m}^{-2}$ with 6% of the neutrons having energy greater than 1 MeV. The resulting tritium level was determined to be 2530 appm. Scaling up to a fusion reactor with 50 Mg of beryllium exposed to 3 MWy m^{-2} results in the production of 5.5 kg of tritium. This is a sizeable quantity of tritium. The relevant question is whether this tritium would be released during normal operation of the fusion plant. Baldwin and Billone [86] examined exactly that question in their experiment. The samples containing the 2530 appm of tritium were heated in stepped anneals to determine the release rate of tritium from beryllium materials with different densities. The annealing began with a very long anneal at 773 K, and the temperature was increased in increments of 100 K. For each temperature, there was a non-diffusional burst of release followed by a rapid decrease in the release rate. The release behavior for the different materials was similar, but the fractional release was greater for the less dense materials. Andreev, *et al.* [87] irradiated hot pressed beryllium at 373 K. After neutron irradiation, thermal desorption spectroscopy was used with a heating rate of 10 K s^{-1} . Release began to occur at approximately 773 K. The temperature at which maximum release occurred depended on the neutron fluence. The sample irradiated to a fluence of $3 \times 10^{25} \text{ n m}^{-2}$ had a peak release at 1080 K, while the sample irradiated to the higher fluence of $1 \times 10^{26} \text{ n m}^{-2}$ exhibited a peak release at the lower temperature of 1030 K. The authors examined the microstructure of the samples after the release anneals. If the anneal was stopped at 973 K, pores with a diameter of 2 to 16 μm were formed. If the anneal was taken to 1373 K, the pore diameters increased to 25 to 30 μm .

Due to the toxicity of beryllium, there have been relatively small numbers of experiments performed on the behavior of hydrogen isotopes in beryllium. The apparent diffusion coefficient of hydrogen in beryllium is strongly affected by purity levels. The values determined for the solubility of hydrogen in beryllium all fall within one order of magnitude even though the apparent activation energy differs by 96 kJ mol^{-1} . Implantation of hydrogen into beryllium results in the formation of bubbles and eventually open channels or porosity. Connection of the porosity to the surface facilitates the release of hydrogen from the beryllium as the particle fluence is increased. The tendency to form bubbles would suggest that the solubility of hydrogen in beryllium is extremely small. It is possible that the values determined for the solubility of hydrogen in beryllium actually represent hydrogen absorbed on the external surface and on grain boundaries. The measured diffusivity may represent migration along grain boundaries. More experiments, and experiments with single crystals, are needed to answer some of these problems. For beryllium used for long times in future fusion devices, tritium produced by neutron reactions on the beryllium is likely to dominate tritium retention in beryllium. Tritium inventory from eroded beryllium codeposited with tritium may play a strong role in tritium inventory, but that effect is not covered in this review.

4.116.3.2. Structural Materials

Structural materials for a fusion reactor are simply those that comprise a majority of the plant. They are not directly exposed to the plasma, but most are exposed to high doses of neutrons and electromagnetic radiation. Many of these materials are used in the reactor blanket where the tritium is bred by the nuclear reaction ${}^6\text{Li}(\text{n},\alpha){}^3\text{H}$. It is in the blanket and in the fuel reprocessing area that the structural materials are most likely to be exposed to tritium. Lets look at the different materials that might be used as structural materials and examine their tritium permeation characteristics.

4.116.3.2.1. *Austenitic stainless steels*

Austenitic stainless steels have been used extensively as a construction material for nuclear reactors, particularly type 316 austenitic stainless steel. The type 300-series austenitic stainless steels (Fe-Cr-Ni) have relatively high nickel content (commonly 8-14 wt%), which is a detriment for fusion applications for several reasons including the susceptibility of nickel to activation (induced radioactivity) [88-90]. The so-called prime candidate alloy (PCA) is a variant of type 316 austenitic stainless steel modified for fusion applications (although interestingly enough with higher nickel content); from a permeation perspective PCA is anticipated to behave essentially the same as conventional type 316 alloys [91].

The solubility and diffusivity of hydrogen and its isotopes through austenitic stainless steels has been extensively studied, this brief review focuses on the results for type 300-series alloys from gas permeation experiments, which is also reviewed in Ref. [1]. The characteristics of hydrogen transport in austenitic stainless steels is independent of deformation when the deformation does not induce martensitic transformations [92-94]. The transport properties are also relatively insensitive to composition for the type 300-series alloys [1].

The most common type 300-series austenitic stainless steels are metastable, meaning that deformation can induce the formation of martensite in the austenitic matrix. This is important because strain-induced martensite has been shown to have a much higher diffusivity for hydrogen and its isotopes than austenite [95, 96]. This has implications on the apparent solubility as well. The stability of austenitic stainless steels with respect to the formation of strain-induced martensite increases most notably with nickel and nitrogen content (although other alloys also participate [97]). Therefore, effects of strain-induced martensite are most apparent on the low-nickel type 300-series alloys, such as type 301 and 304, although type 316 austenitic stainless steel can transform (e.g., if nickel content is relatively low or if deformed at subambient temperature).

The Fe-Cr-Mn austenitic stainless steels have been considered as substitute for the more common grades of austenitic stainless steels since they have only nominal nickel content [88-90], although low-activation ferritic/martensitic steels have received more attention (see subsequent section). Alloys that have been considered typically contain both Cr and Mn in the range 10-20 wt%, often with small amounts of other alloying elements (Ref. [90] provides a list of a number of alloys that have been explored for fusion applications). Unlike the Fe-Cr-Ni austenitic stainless steels, there are few reports of transport properties for the Fe-Cr-Mn austenitic alloys; data for oxidized Fe-16Cr-16Mn are reported in Ref. [98].

< figure 10 here >

Reported values of hydrogen diffusivity in austenitic stainless steels are less consistent than permeability as a consequence of surface effects and trapping, as mentioned above and elsewhere [1]. Figure 10 shows the reported diffusivity of hydrogen from a number of studies where special precautions were taken to control surface conditions. The activation energy for diffusion is relatively large for austenitic stainless steels ($E_D = 49.3 \text{ kJ mol}^{-1}$), thus the diffusivity is sensitive to temperature, approaching the values of the ferritic steels at very high temperature ($>1000 \text{ K}$), while being many orders of magnitude lower at room temperature.

Studies on austenitic steels have shown that hydrogen transport and dissolution are independent of whether the microstructure is annealed or heavily cold-worked (when the microstructure is stable with respect to phase change) [92, 93]. However, the diffusivity of hydrogen in ferritic phases (e.g., ferrite and α -martensite) tends to be greater than in the austenitic phase, especially near room temperature. Thus, residual ferrite in wrought austenitic stainless steels and ferrite that forms in welds of austenitic stainless steels can result in a fast pathway for the transport of hydrogen and its isotopes at low temperatures. Strain-induced α -martensite is also a ferritic phase that forms in metastable austenitic stainless steels when heavily deformed (type 304 and 321, as well as type 316 deformed at low temperature) and will greatly increase the permeability and diffusivity of hydrogen in the alloy [94, 95].

< figure 11 here >

The solubility of hydrogen and its isotopes in the Fe-Cr-Ni austenitic stainless steels is high relative to most structural materials. Compilation of data from gas permeation studies shows that most studies are consistent with one another [92, 93, 95], while studies that considered a variety of alloys within this class show that the solubility of hydrogen is essentially the same for a wide range of type 300-series austenitic stainless [92, 93, 95]. The heat of solution of hydrogen in austenitic stainless steels is relatively low ($\Delta H_s = 6.9 \text{ kJ mol}^{-1}$), thus the equilibrium content of hydrogen in the metal remains high even at room temperature. The solubility of hydrogen and its isotopes is plotted in Figure 11, while Table 1 lists the recommended transport properties for austenitic stainless steels (and a number of other metals and alloys). While the solubility appears to be insensitive to composition for the type 300-series alloys, the Fe-Cr-Ni-Mn alloys (which have not been widely considered for fusion applications) feature solubility that is more than 50% higher [1].

It is important to re-iterate that hydrogen solubility is generally determined indirectly from the ratio of the permeability and the diffusivity. Thus, the accuracy of the solubility determination depends on the measurement of the diffusivity (permeability measurements are less sensitive to kinetic effects because it is a steady-state measurement). In particular, determinations of the diffusivity of hydrogen and its isotopes can be strongly influenced by the surface condition of the specimen in gas permeation tests, therefore the quality of reported solubility relationships depends on establishing diffusion-limited transport with the experimental methods that are employed (and appropriate analysis of the flux transients) [1]. In addition, trapping affects diffusivity and must, therefore, be mitigated in order to produce solubility relationships that reflect the lattice dissolution of hydrogen and its isotopes in the metal.

The primary traps in type 300-series austenitic stainless steels are dislocations with relatively low binding energy: approximately 10 kJ mol^{-1} [99]. Therefore, the amount of trapped hydrogen (in the absence of irradiation and implantation damage) is relatively low at elevated temperature. Moreover, due to the high solubility of hydrogen and its isotopes in austenitic stainless steels, the density of trapping sites would need to be impractically high to measurably increase the inventory of hydrogen and its isotopes in the metal [20]. For these reasons, trapping from a microstructural origin is anticipated to have little if any impact on the transport of hydrogen and its isotopes in austenitic stainless steels at temperatures greater than ambient.

The recombination-rate constant (k_r) for austenitic stainless steels near ambient temperature is typically less than about $10^{-9} \text{ m}^4 (\text{s} \cdot \text{mol H}_2)^{-1}$ [100]. At higher temperature ($\sim 700 \text{ K}$), the value

varies between approximately 10^{-5} and 10^{-7} $\text{m}^4(\text{s}^{-1}\text{mol H}_2^{-1})$ depending on the surface condition [80, 100-103].

Austenitic stainless steels show significantly lower permeability of hydrogen than other structural steels, particularly at low temperature. The low permeability can be attributed to the low diffusivity in these steels. The solubility of hydrogen and its isotopes, on the other hand, is large in austenitic stainless steels compared to other structural steels and the heat of dissolution is significantly lower than other metals. Thus, the tritium inventory in austenitic stainless steels can be relatively high even at low temperature. The low binding energy associated with trapping of hydrogen in austenitic stainless steel, combined with the high solubility, equates to essentially no contribution of trapping to the hydrogen inventory.

4.116.3.2.2. Ferritic/martensitic steels

There is significant interest in reduced activation ferritic/martensitic (RAFM, also called RAM) steels to replace nickel-bearing austenitic stainless steels in reactor applications [104]. There are many RAFM steels that have been proposed and investigated in the literature specifically for fusion applications; these typically contain between 7 to 10 wt% Cr, relatively low carbon (<0.15 wt% C), and controlled alloying additions to bolster structural properties while minimizing activation (e.g., additions of W and Nb, reductions of Ni and Mo content). The transport of hydrogen and its isotopes have been extensively studied in MANET (MArtensitic for NET, including the so-called MANET II) and modified F82H (generally referred to as F82H-mod). Some of the other designations of RAFM steels that can be found in literature include EUROFER 97, Batman, OPTIFER-IVb, HT-9, grade 91, JLF-1 and CLAM steel.

In general, studies of RAFM steels report relatively consistent transport properties of hydrogen and its isotopes; some of these studies are reviewed in Ref. [105]. Despite the consistency of the data available in literature from several research groups, few studies verify the expected pressure dependence of the transport properties that is expected for diffusion-controlled transport. Pisarev and co-workers have suggested that the literature data may underestimate diffusivity and solubility due to surface limited transport [106, 107]. Similar suggestions have been presented to explain some of the data for the austenitic stainless steels [1]; however, the work on austenitic stainless steels has been cognizant of the issues with surface effects; generally surface effects are mitigated by coating specimens with palladium or other surface catalyst. Such precautions have not been systematically employed for permeation studies of the RAFM steels, although the need to control the surface condition (and confirm the square root dependence on pressure) has widely been acknowledged [29, 30, 105, 108]. While the apparent transport properties in the absence of trapping are relatively consistent for all the RAFM steels, the issue of surface effects and the suggestions of Pisarev, *et al.* need further validation in the literature because the transport of tritium is less likely to be affected by surface conditions.

< figure 12 here >

The diffusivity of hydrogen is shown in Figure 12 along with an average relationship (Table 1). The literature data generally are within a factor of 2 of the recommended relationship. The MANET alloys tend to have lower diffusivity of hydrogen and its isotopes than F82H-mod. Differences in permeability between these two alloys has been attributed to Cr content [29, 30], however, a clear correlation of transport properties with Cr content cannot be established based

on existing data [109]. At temperatures less than about 573 K the apparent diffusivity is significantly less than the exponential relationship extrapolated from higher temperature. This is attributed to the effect of trapping on the transport of hydrogen and its isotopes.

< figure 13 here >

The reported values of apparent solubility of hydrogen and its isotopes in RAFM varies by very little in the temperature range from 573 to 873 K. Pisarev and co-workers report values that are 3 to 4 times higher based on their assessment of surface effects. Here we recommend a relationship for the apparent solubility (Table 1) that is consistent with the majority of the literature data with $\Delta H_s = 28.6 \text{ kJ mol}^{-1}$, which is based on simple curve fitting of the data shown in Figure 13. The values of the solubility are about an order of magnitude less than the austenitic stainless steels in the temperature range between 500 and 1000 K, although the solubility of hydrogen is more sensitive to temperature for the RAFM steels since ΔH_s is 4 times the value for the austenitic stainless steels.

The trapping characteristics of the RAFM steels have been estimated for several alloys [19, 105, 108, 110-113]. Although binding energies and densities of hydrogen traps vary substantially, the majority of reported values for RAFM steels are in the range 40 to 60 kJ mol^{-1} and 10^{-3} to 10^{-5} traps per metal atom, respectively. The traps are attributed primarily to boundaries [105] and result in a significant reduction in the apparent diffusivity at temperature less than about 573 K. At higher temperature, the traps are essentially unoccupied and do not affect diffusion [20].

The measured recombination coefficient is many orders of magnitude lower than theoretical predictions; moreover, the measured values can also vary substantially from one study to the next [105, 114, 115]. Measured values for the recombination coefficient for deuterium on MANET alloys are approximately in the range 10^{-2} to $10^{-4} \text{ m}^4(\text{s}^{-1}\text{mol H}_2^{-1})$ for the temperature range 573 to 773 K [114, 115]. Oxidation of MANET results in lower values: $k_r \approx 10^{-6} \text{ m}^4(\text{s}^{-1}\text{mol H}_2^{-1})$ [115].

The diffusivity and solubility of hydrogen and isotopes are consistently similar for all the RAFM steels that have been tested for fusion applications. RAFM steels show relatively rapid diffusion and low solubility of hydrogen and its isotopes at ambient temperature. The diffusivity is six orders of magnitude greater than the austenitic stainless steels at 300 K, while the solubility is more than three orders of magnitude lower than the austenitic stainless steels. The diffusivity of hydrogen and its isotopes is not strongly sensitive to temperature compared to most other metals. On the other hand, the heat of solution (ΔH_s) for the RAFM steels is quite large, thus the solubility of hydrogen approaches that of austenitic stainless steels at temperatures greater than 1000 K. Consequently, at elevated temperature (e.g., greater than 700 K), the permeability is less than an order of magnitude greater than the austenitic stainless steels and within a factor of five at temperature greater than 1000 K. Trapping is significant in the RAFM steels at temperature less than about 573 K, thus the apparent diffusivity is much lower than expected from tests that are performed at higher temperature.

4.116.3.2.3. V–Cr–Ti alloys

BCC-structured V–Cr–Ti alloys (particularly composition ranges of around V–4Cr–4Ti and V–15Cr–5Ti) have low neutron cross sections and the isotopes that do form with neutron capture have short half lives (^{51}V has a half-life of less than 4 minutes). These characteristics, along with

reasonable operating temperatures (limited by radiation hardening and helium bubble formation to $\approx 575\text{--}775\text{ K}$ [116]), make V–Cr–Ti an attractive material for first walls and blankets, but the tritium retention characteristics of vanadium alloys leave much to be desired. Vanadium has a large solubility for hydrogen and a very large diffusion coefficient for hydrogen. These two traits make the permeability of H in V comparable to that of Ti and Pd [117]. Vanadium absorbs hydrogen exothermically. Additions of Cr tend to increase this energy, while Ti additions tend to decrease it and, to first order, alloys with roughly equal and small amounts of Cr and Ti (such as V–4Cr–4Ti) are assumed to react similarly to hydrogen isotopes as pure V [116]. Vanadium alloys form hydrides below $\approx 450\text{ K}$ [116], which is below the typical operating temperatures.

< figure 14 here >

The diffusivity of H in V is $\approx 10^{-8}\text{ m}^2\text{s}^{-1}$ in the range of operating temperatures, a larger value than in most metals [116]. There has been extensive experimental measurement of several V–Cr–Ti alloys using different hydrogen isotopes. These are summarized in Figure 14. Schaumann, *et al.* [118] and Cantelli, Mazzolai and Nuovo [119] independently measured the diffusivity of both protium and deuterium in pure V after charging them with gas at $\approx 775\text{ K}$ using the Gorsky effect. Both groups found that the prefactor did not depend strongly on the isotope, whereas the activation energy did. This is contrary to the common naïve expectation, where the activation energies would be identical and the prefactors would differ by a factor of the square root of the mass. The two groups also each reported a deviation from exponential behavior at lower temperatures, which could be attributed to some combination of surface effects, trapping, and a V–H phase transition at $\approx 200\text{ K}$ [119]. However, deviation from Arrhenius behavior is common in BCC metals [120] and has been reported in a number of studies on V. The transition temperature from exponential behavior varies widely with the technique used to measure diffusivity and the group that measures it [118, 119, 121–126], and has been as high as 813 K when measuring uncharged specimens using the absorption technique [121]. This supports the notion that much of the deviation reported in the literature may be due to surface recombination limitation at lower temperature. At lower temperatures, there was an increased deviation in the measured $D_{\text{H}}/D_{\text{D}}$ from $\sqrt{2}$, which has also been observed by others [125, 127] and in the diffusivity of T [128]. The heavier hydrogen isotopes do not diffuse much slower than predicted until temperatures below ca. 373 K , thus the physics associated with deviations from the predictions of classical rate theory cannot be exploited for the use in fusion applications. The electrochemical pulse experiments of Boes and Zuchner [129] derived an activation energy that is twice as large using the electrochemical pulse method, which was also supported by absorption experiments by Eguchi and Morozumi [121]. Both techniques are influenced by the surface, while Gorsky effect measurements and electrical resistivity measurements are only influenced by the bulk [120]. The absorption experiments also indicated that the hydrogen diffusion coefficient in V alloys is decreased by additions of Cr (as well as Fe and Nb), but that it could be increased by large Ti additions, which is thought to be due to electronic contributions [121]. Most other experiments have found that moderate amounts of Ti decrease the hydrogen diffusion coefficient much more than Cr is able to [120, 126]. Ti's strong ability to trap hydrogen isotopes may explain the discrepancy in these measurements. Increasing Ti content decreases the $D_{\text{H}}/D_{\text{D}}$ ratio, while increasing Cr content increases the ratio [126].

< figure 15 here >

While the solubility for H in V is smaller than that in either Zr or Ti, it is still very large, being greater than the value in Pd and much greater than the value in the other structural metals considered here (Figure 15). The reported hydrogen lattice solubilities in Zr alloys are in reasonable agreement, regardless of composition [117]. Alloying additions do, however, change trapping in the alloy.

Ti has a higher heat of solution for H than V and Ti [125] additions increase the lattice parameter of V [120]. However, Ti is a much stronger trap than other elements that increase the lattice parameter as much or more (including Nb, Mo, and Zr) [120]. Pine and Cotts [126] assert that Ti solute atoms not only trap hydrogen isotopes at nearest-neighbor interstitial sites, but also trap H substitutionally. They demonstrated that the binding energy varied from 3 kJ mol⁻¹ in V-3Ti to 9.84 kJ mol⁻¹ in V-8Ti. The trapping energy for D is larger than H for both alloys. However, it should also be noted that there is considerable short-range ordering in V-Ti alloys with more than ca. 4 at.% Ti [120]. This ordering means that trapping will not obey Oriani-type behavior, where trapping would be linearly dependent on the number of solute atoms, because the solid solution is not random. Cr, Fe, and, Cu all reduce the lattice parameter of V and the diffusivity change in alloys containing these elements is also much lower than alloys with Ti [120]. In fits to the apparent diffusivity in tritium diffusion experiments in ternary V-Cr-Ti alloys, Hashizume, *et al.* [122] show that, in addition to single Ti atoms, the most likely secondary trap is not Cr. Instead, the secondary trap has much higher energy and a lower concentration when compared to the monomer Ti trap. They also speculated that this was due to solute dimers and larger clusters. Other defects, such as dislocations, may still be effective traps at 773 K [130]. As with other materials, V can be damaged by radiation, and this will likely be the dominant trap in fusion reactors. [131, 132]

The recombination coefficient for H is over five orders of magnitude slower in V than in Ni in the range of operating temperatures, and is relatively insensitive to the surface concentration of sulfur [116]. Because of this and the high diffusivity of tritium, release is recombination-limited in V alloys. Deuterium ion-driven permeation experiments of V-15Cr-5Ti have estimated the recombination rate coefficient to be $2.4 \times 10^{-29} \text{ m}^4 \text{ s}^{-1}$ [133] (although this measurement differs by three orders of magnitude lower than measurements on more dilute alloys [134] and two orders of magnitude higher than measured in pure V [135]). It should be noted that most measured recombination rates are lower bounds due to surface oxides. In environments where this native oxide layer may be damaged (such as by radiation in a fusion reactor), the actual recombination rate may be larger [132].

V-Cr-Ti alloys have hydrogen permeabilities that are at least two orders of magnitude more than nearly any other blanket material. The ongoing studies on permeation barriers may allow mitigation of this significant disadvantage so that V's positive traits in a high-energy neutron environment can still be utilized.

4.116.3.2.4. Zirconium alloys

Zirconium alloys are corrosion resistant in aqueous environments and have low neutron cross sections [136]. However, Zr readily forms embrittling hydride precipitates. Zirconium alloys oxidize and the surface ZrO₂ may be an effective permeation barrier, preventing both hydrogen release and formation of detrimental hydrides. Andrieu, *et al.* [137] demonstrated that the rate of tritium release of zircaloy-4 (Zry4) decreased substantially upon oxide formation in tritiated water.

< figure 16 here>

Zirconium has multiple phases in some potential temperatures of interest: at 833 K, alpha, beta, and gamma Zr coexist in equilibrium. Most solubility and diffusivity studies have been conducted on the single-phase alpha-Zr; generally at 773 K and below (Figure 16). Above this temperature, Zr alloys dissolve up to 50 at.% H and this solubility decreases rapidly with decreasing temperature, causing hydride precipitates within the alloys. The solubility has been found to vary slightly with alloying content. Yamanaka, *et al.* [138] note that the solubility in the beta phase decreases with alloying additions, while the solubility in the alpha phase increases with alloying additions.

The solubility of H in ZrO₂, regardless of crystal structure (10^{-4} - 10^{-5} mol H per mol oxide), is much smaller than the base metal and is even smaller than that in Al₂O₃. Alpha ZrO₂ exhibits a solubility almost an order of magnitude smaller than beta ZrO₂ [139].

< figure 17 here>

Greger, *et al.* [140] have reviewed H diffusion in Zr. The diffusivities reported in studies they cite and in others is plotted in Figure 17. At 623 K, the diffusivity of hydrogen in Zr is 10^{-10} m²s⁻¹ [137, 140-144], while the diffusivity in ZrO₂ is only 10^{-19} - 10^{-20} m²s⁻¹ [137, 141, 145]. Austin, *et al.* [141] were able to measure the diffusivity in both alpha and beta phases by measuring the activity, due to tritium, in tomographic slices of samples. The diffusivity values do not have a very strong dependence on crystallographic orientation or on alloy composition.

Based on observations of tritium segregation to some precipitates [137, 142], many authors [137, 146, 147] argue that intermetallic precipitates in zircaloy could be paths for short-circuit diffusion due to large reported values for solubility and diffusivity in some of these phases. However, these quantities appear to be relatively large for the Zr-matrix material. Further, autoradiography shows depletion in some Fe-rich precipitates and at 623 K, the diffusivity in ZrFe₂ is 2.5×10^{-11} m²s⁻¹, slower than bare Zr [148]. The permeability values through hydrides might be larger due to the high solubility of hydrogen isotopes the hydride phase. However, the volume fraction of hydrides tends to be small and the activation energy has been shown to be independent of the presence of the hydride [149].

Zirconium alloys that lack an oxide layer are not useful in hydrogen environments that exceed the solubility of H in Zr, due to hydride formation. At relatively low use temperatures (<623 K), and in aqueous or otherwise oxidizing environments, zirconium oxide is able to grow and is an effective barrier against the permeation of hydrogen. Above this temperature, the integrity of the oxide layer cannot be maintained and the effective permeation of hydrogen isotopes is increased substantially.

4.116.3.2.5. Other structural metals

- Aluminum

The permeability of hydrogen isotopes thorough aluminum is smaller than most metals. This is due to a very low intrinsic solubility and a moderate H diffusivity. Young and Scully [150] reviewed the diffusivity of hydrogen in Al and discussed the reasons for the wide range of

reported values. A majority of hydrogen present in Al alloys at lower temperatures is trapped at defects and alloying content tends to increase the solubility for H in Al slightly [150-152].

Application of aluminum alloys in fusion reactors is limited by their low melting temperature (933 K for pure Al or significantly lower for some alloys), the formation of embrittling intermetallics when layered on other metals, and the difficulty of joining aluminum alloys (due to the native oxide layer). The thermal limitation is significant because precipitates in conventional Al alloys coarsen or dissolve above 450 K and most conventional alloys are not very resistant to creep deformation. Few studies have been made to date on Al alloys for use at temperatures greater than about 450 K. Because many Al-containing intermetallics and aluminum oxide also have low hydrogen permeability and do not have the same thermal limitations as metallic Al, it has been proposed that they be used as hydrogen isotope barriers [110].

- Nickel

The permeation of hydrogen and its isotopes in nickel has been extensively studied. The results from Louthan, *et al.* [153] provide a good estimate of the transport properties. They found that cold-worked nickel displays higher permeability to hydrogen, speculating that diffusion is enhanced along dislocation networks. Louthan also measured permeation in high-pressure gaseous hydrogen isotopes [4], showing that the transport is not dependent on concentration (and that Sievert's Law is appropriate at elevated pressure). Normalization of nickel's permeation [4] and diffusion [3] by the mass ratio (equation 3) has been shown to provide good agreement for all three isotopes.

- Copper

There are numerous reports of permeability of hydrogen in copper; the gas permeation results of Begeal [154] are suggested here. Caskey and co-workers [155] found that the diffusivity of hydrogen in copper depends on the oxygen content and, consequently, that the effective diffusivity can be much lower than the lattice diffusivity. Nevertheless, the reported diffusivity is consistent among a number of reports [3, 154-157].

4.116.3.3. Barrier Materials

4.116.3.3.1. Oxides

Most metals form a native oxide layer in the presence of oxygen. Oxides have very low permeabilities for hydrogen isotopes generally, and native oxide layers may reduce permeability by about an order of magnitude [158]. The coefficient for thermal expansion is often very different from the underlying metal. This can cause cracks and spalling, which can reduce the effectiveness of the barrier. In environments that are aqueous or are subjected to elevated temperature in the presence of oxygen, the oxide layer may be replenished, and may even grow and coarsen. In addition to native oxides, an oxide layer might be deposited onto the base metal or the base metal might be dipped or otherwise coated with a second metal, which forms a low-permeability oxide. Such coatings may reduce hydrogen permeability by five orders of magnitude or more [159]. Chromia, alumina, and rare-earth oxides have been studied extensively.

The very low dissociation pressure of Cr_2O_3 makes it a common native oxide on steels when allowed to form at elevated temperatures and relatively low oxygen partial pressures [160].

Chromia is a better barrier (offering a permeation reduction of about an order of magnitude [158, 161]) than various Cr_2MO_4 spinels that may also form [160]. Chromia is also present in mixed oxides in chemical densified coatings, which help to give reduction factors of four orders of magnitude [162].

Aluminum forms a self-passivating native oxide that has been shown to be highly resistant to hydrogen isotope permeability, due to a very low solubility for hydrogen. Alumina may also be formed by dipping cleaned stainless steel in aluminum and oxidizing it. This hot-dip aluminizing processing is simple and generally forms coatings which have excellent adhesion properties and offer permeability reduction factors of at least one, and sometimes more than five orders of magnitude [158, 163].

< figure 18 here>

< figure 19 here>

The basic properties of hydrogen transport in alumina have been characterized and are presented in Figure 18 and Figure 19. Roy and Coble [164] hot-isostatically pressed powders that were over 99.99% pure powder and charged it with hydrogen at elevated temperature to calculate the solubility as $K=12.5\exp(-8,024/T) \text{ mol H}_2 \text{ m}^{-3} \text{ MPa}^{-1/2}$. Fowler, *et al.* [165] obtained diffusion coefficients for single crystal, polycrystalline, and powdered alumina and alumina that was doped with MgO. They observed faster diffusion in powdered specimens, suggesting that grain boundaries may provide short-circuit diffusion paths. They also noted that the diffusivity of MgO-doped alumina was four to five orders of magnitude greater than pure alumina. This suggests that the purity of barrier coatings matter a great deal and transmutation of barriers in a fusion environment may increase the permeability from the ideal case measured in the laboratory.

Yttria and ErO have been deposited on specimens through a number of physical deposition techniques, including plasma spray, arc deposition, and sol-gel deposition [166-168]. The advantage of these oxides is not the magnitude of permeation reduction (one to three orders of magnitude), but in their high thermal and mechanical stability in a reducing atmosphere.

4.116.3.3.2. *Aluminides*

In addition to forming Al_2O_3 , which is known to decrease hydrogen permeation, aluminization of steels forms aluminide intermetallics that are believed to also lower permeability. Most aluminization processes also lead to the formation of surface Al_2O_3 and, to our knowledge, no permeation measurements on oxide-free aluminides has been performed. However, the different processes lead to oxide scales of differing composition, thickness, and defect density, and the PRF may not be attributable to oxides alone. Steels have been aluminized by the hot dip process (described above), as well as by various CVD, spray, packed-bed, and hot isostatic pressing (HIP) techniques. For those techniques that lay down a substantial amount of materials that does not react with the matrix (such as HIP), an Al-containing Fe alloy can be used in preference to Al to offer higher temperature barrier performance [169]. Oftentimes, the aluminized layer will be made up of mixed FeAl , FeAl_2 , Fe_2Al_3 , Fe_2Al_5 , FeAl_3 , and even $\text{Fe}_4\text{Al}_{13}$ intermetallics [170]. Nickel, Cr, and mixed-aluminides are also formed [171, 172]. The Al-rich intermetallics segregate to the surface and aluminized material will often have a mixed oxide scale that is rich in Al_2O_3 [173, 174]. Permeation reduction factors (PRFs) vary between 10 and 10,000 [158, 175]. The PRFs are generally larger than for a pure Al layer, and barriers containing a clean

Al₂O₃ surface often have the greatest PRF [176]. It should be noted that Al additions can also stabilize ferrite in some austenitic stainless steels, producing a duplex microstructure and an increased permeation [177].

4.116.3.3.3. Nitrides

As with oxides, either the native nitrides of the base metal or depositions of other nitrides can be made to serve as barriers. One of the most common native nitrides is Fe₂N, which forms when the upstream face of steel samples are nitrided and reduces permeability by one to three orders of magnitude [178-180].

After oxides and aluminide, TiN coatings are one of the most researched barriers due to their good adhesion and the ease of deposition [158]. Reported PRFs for nitride barriers vary widely, from less than an order of magnitude to six orders of magnitude. TiN barriers reduce permeability the most when they are placed on the high-pressure side of samples, and much less change in permeation is observed when they are placed downstream [181, 182].

Boron nitride has been shown to reduce the permeability of H in 304SS by one to two orders of magnitude [158, 183]. It forms both cubic and hexagonal structures. Checchetto, *et al.* [184] noted that the hexagonal structures have a greater amount of hydrogen isotopes (due to a larger number of trapping sites; particularly dangling B and N bonds), but also a greater diffusivity of hydrogen. The latter effect may be due to preferential diffusion along the *a* direction of the hexagonal lattice.

Bazanella, *et al.* [185] found that a 1.7 micron (Al,Ti)N coating reduces the deuterium permeability of 0.1 mm thick 316L by 2-3 orders of magnitude. From permeation transients, they speculated that this reduction was primarily due to the very low diffusivity of D in (Al,Ti)N.

4.116.3.3.4. Carbides

The only reported data on the solubility of hydrogen in boron carbide is that by Shirasu, *et al.* [186]. They exposed crystals of boron carbide to hydrogen gas at various temperatures and pressures for 20 hours, and subsequently outgassed them during anneals where the temperature was linearly increased at 20 K per minute up to 1,273 K. The uptake was seen to increase with the square root of pressure, and to decrease with increasing temperature (exothermic). Their solubility can be given by the expression $S = 3.8 \exp(3,590/T) \text{ mol H}_2 \text{ m}^{-3} \text{ MPa}^{-1/2}$. Schnarr and Munzel [187, 188] measured the diffusivity of tritium in both irradiated and unirradiated boron carbide. While the actual expression for the diffusivity for each case was not given, it can be extracted from the figures. The approximate diffusivity for unirradiated boron carbide is $D = 1.23 \times 10^{-11} \exp(-9,720/T) \text{ m}^2 \text{ s}^{-1}$ and $D = 4.3 \times 10^{-8} \exp(-26,000/T) \text{ m}^2 \text{ s}^{-1}$ for the irradiated material. It was noted that the apparent diffusivity decreased with increasing radiation damage until the percentage of ¹⁰B exceeded 10%. Elleman, *et al.* [189] used the ⁶Li-neutron reaction to generate tritium profiles in samples of boron carbide. Diffusivities were determined by examining the rate of release of the tritium during isothermal anneals at elevated temperatures. Their diffusivity was given as $D = 1.1 \times 10^{-10} \exp(-8,450/T) \text{ m}^2 \text{ s}^{-1}$.

< figure 20 here >

The diffusivity and solubility of hydrogen in silicon carbide has been measured twice by Causey, *et al.* [190, 191]. In the first set of experiments [190], various grades of silicon carbide were implanted with tritium using the neutron reaction with ^6Li on the sample surfaces. The diffusivity for each material was then determined by fitting the release curves determined during isothermal anneals to those predicted by the analytical solution to the diffusion equation. The results were seen to differ strongly depending on the type and purity of the silicon carbide. As an example, the measured diffusivity in hot pressed and aluminum-doped alpha silicon carbide was approximately five orders of magnitude greater than that of vapor deposited beta silicon carbide at 1273 K. The lowest diffusivities were reported for vapor deposited beta silicon carbide and single crystal alpha silicon carbide. In all cases, the activation energy of the diffusivity was greater than 2 eV (suggesting chemical bonding plays a strong role in the diffusion). For the diffusion of tritium in vapor deposited silicon carbide, the diffusivity was given as $D=1.58 \times 10^{-4} \exp(-37,000/T) \text{ m}^2 \text{ s}^{-1}$. Deuterium solubility was also determined for the vapor deposited silicon carbide. The values were determined by exposing samples at elevated temperatures to deuterium gas followed by outgassing to determine the amount of uptake. Because equilibrium retention was not obtained in the experiments, inherent in the calculations was the assumption that the diffusivity values determined in the implantation experiments were valid in the gaseous uptake experiments. The amount of uptake was assumed to be the product of diffusivity times the solubility times the sample area times the square root of pressure. The solubility was given as $S=1.1 \times 10^{-3} \exp(+18,500/T) \text{ mol H}_2 \text{ m}^{-2} \text{ MPa}^{-1/2}$. Again, the negative value for the activation energy would suggest chemical bonding of the hydrogen to the host material. In the later work by Causey, *et al.* [191], vapor deposited silicon carbide was again tested. In these experiments, the implantation of energetic particles into the silicon carbide was avoided. Samples were exposed to gas containing 99% deuterium and 1% tritium at a temperature of 1573 K for 1 hour. The samples were subsequently outgassed at temperatures from 1373 K to 1773 K. The outgassing rates were then fitted to release curves predicted by the solution to the diffusion equation to determine the diffusivity. In this case, the diffusivity was given by the expression $D=9.8 \times 10^{-8} \exp(-21,870/T) \text{ m}^2 \text{ s}^{-1}$, one to two order of magnitude faster than the values determined earlier with energetic particles [190]. The solubility was also determined in this study. Samples were exposed to the deuterium/tritium gas at temperatures from 1273 K to 1873 K for sufficient times to achieve equilibrium loading. The samples were then outgassed to determine this equilibrium amount. The expression for the solubility in this case was $S=2.2 \times 10^{-2} \exp(+7,060/T) \text{ mol H}_2 \text{ m}^{-3} \text{ MPa}^{-1.2}$. This solubility is one to two orders of magnitude smaller than the one determined in the earlier experiments [190]. If one assumes the migration of hydrogen in silicon carbide to occur along active sites on the edges of the crystallites, it is not unexpected that radiation damage produced by the implantation of energetic particles would increase the apparent solubility and proportionately decrease the apparent diffusivity. If hydrogen can only exist on the grain boundaries by being attached to trap sites, higher trapping means higher apparent solubility. Conversely, higher trapping means slower diffusion. It was the apparent higher solubility on small grained samples that led Causey, *et al.* [191] to propose the trap controlled grain boundary diffusion model.

The permeation of hydrogen isotopes through silicon carbide has been measured by several groups [192-194]. Verghese, *et al.* [193] measured the permeation of a hydrogen/tritium mixture through a KT silicon carbide tube that was manufactured by wet extrusion and sintering. The permeability reported for the experiments is given by $P=3.8 \times 10^8 \exp(-66,000/T) \text{ mol H}_2 (\text{m}^{-1} \text{ s}^{-1} \text{ MPa}^{-0.5})$. Sinharoy and Lange [192] measured the permeation of hydrogen through a tungsten tube with a CVD coating of silicon carbide. The retarding effect of the tungsten was taken into consideration in the calculation. The recorded

permeation for these experiments was $P=2 \times 10^{-4} \exp(-6,830/T) \text{ mol H}_2(\text{m}^{-1}\text{s}^{-1}\text{MPa}^{-0.5})$. Yao, *et al.* [194] performed permeation experiments on a steel sample that had been RF sputter-coated with silicon carbide. The thickness of the coating was estimated to be 1.3 μm thick and contained several percent oxygen and traces of iron. The coating was seen to decrease the permeation rate of steel by about two orders of magnitude, but did not change the activation energy. In this case, the coating was clearly porous, and the reduction in permeation was simply due to a reduction in the effective permeation surface area. The plot of the permeation values for the vapor deposited silicon carbide by Causey, *et al.* [191] (calculated as the product of diffusivity times solubility), KT silicon carbide by Verghese, *et al.* [193], and CVD silicon carbide by Sinharoy and Lange [192] is shown in Figure 20. The differences in the absolute values of the permeability as well as the differences in the activation energy of the process are extreme. It is difficult to even imagine the values are for the same material. In fact, the materials are not the same. As mentioned for the original study by Causey, *et al.* [190], differences in impurities play a significant role in determining the behavior of hydrogen in silicon carbide. If hydrogen does migrate along crystallites edges, impurity metals along those edges reduce the fraction of migrating hydrogen chemically bound to the silicon carbide. Likewise, the apparent diffusivity would be much more rapid. In the case of the permeability measured by Sinharoy and Lange [192] it is difficult to believe that the measured permeation is not really controlled by permeation through the underlying tungsten with the specific surface area limited by the porous silicon carbide coating. The activation energy for the permeation in the report by Verghese, *et al.* [193] is difficult to understand. The value of 555 kJ mol^{-1} is even greater than the chemical bond of hydrogen to carbon [195]. The permeation was seen to vary by as much as an order of magnitude at the same temperature. There is no apparent explanation for the rapid change in permeation with temperature.

Titanium carbide has also been tested as a permeation barrier. Due to adhesion problems with direct deposition on steel, titanium nitride was used as an intermediate layer between the steel and titanium carbide. Forcey, *et al.* [182] measured deuterium permeation through 3 μm thick layers of the combined material on steel and saw a reduction factor of ten over that of steel alone. For the experiments performed over the temperature range of 550 to 740 K, extended defects were listed as the reason for the relatively small improvement over bare steel. Checchetto, *et al.* [181] used ion-beam assisted deposition of TiN-TiC films on steel in their permeation experiments. When the film was deposited on the downstream side, little reduction in permeation was seen. Using the deposited film on the upstream side did yield a PRF of approximately fifty. Shan, *et al.* [196] used a CVD process to deposit their 2.5 μm thick film on steel and noted a permeation reduction of five to six orders of magnitude. It is obvious from these three studies that the deposition of thin films to get theoretically dense layers is very difficult. There is also the question of cracking of such thin films during thermal cycling. This will be discussed later in this chapter.

4.116.3.3.5. Low permeation metals

The permeation of hydrogen and its isotopes through many of the transition metals is lower than that displayed by iron and the ferritic steels; the notable exceptions include groups 4 and 5 as well as palladium. Figure 21 shows the permeability of several metals; the diffusivity and solubility are listed in Table 1 for these metals. In general, the activation energy associated with permeability ($\Delta H_s + E_D$) is larger for the materials with lower permeability and the permeability tends to converge at elevated temperature.

We do not attempt to comprehensively review the data for non-ferrous metals. However, gas permeation studies are considered the standard for transport properties, particularly studies that report permeability, diffusivity and solubility. Permeation of tritium through metals and alloys was reviewed by Steward [197].

- Molybdenum

Several reviews of the literature on hydrogen transport in molybdenum have noted variability of the transport parameters [105, 197, 198]. The reported permeability values are relatively consistent between the majority of studies, while the diffusivity and solubility values range over several orders of magnitude. The results of Tanabe *et al.* [198] are proposed here as they appear to represent nearly upper bounds of both diffusivity and solubility, without overestimating permeability. The study of Tanabe and co-workers also has the advantage that permeability and diffusivity were measured over a wide range of temperature and pressure, confirming the appropriate pressure dependencies of permeability and diffusivity for diffusion-limited transport.

- Silver

The available data for hydrogen permeation through silver are limited. The diffusivity of hydrogen is reported by Katsuta and McLellan [199]. McLellan also reports the solubility of Group IB metals from saturation experiments [200]. Although these saturation experiments do not appear to provide reasonable values for other Group IB metals and are not consistent with other reported solubility measurements [201], Steward, nevertheless, suggests estimating the permeability of hydrogen using these reported relationships [200].

- Platinum

There are relatively few gas permeation studies of platinum. Ebisuzaki, *et al.* report the permeability, diffusivity and solubility of both hydrogen and deuterium through single crystals of high-purity platinum [202]. The permeation of hydrogen in platinum is similar to that in copper.

- Gold

Caskey and Derrick report the permeability of deuterium through gold [203]; Begeal reports a similar relationship [154]. Diffusivity measurements, however, differ depending on the conditions of the measurement and the microstructural state of the gold [203, 204]. Cold-worked gold tends to give a higher activation for diffusion, suggesting that trapping is active to relatively high temperature. Caskey and Derrick speculate that trapping is related to vacancies [203]. The diffusivity in Table 1 is from Eichenauer and Liebscher [205], while the solubility is estimated from this diffusivity and the permeability reported by Caskey and Derrick [203].

4.116.4. APPLICATION OF BARRIERS

4.116.4.1. Expected In-Reactor Performance

< figure 21 here>

< figure 22 here>

< table 1 here>

< table 2 here>

As implied by Figure 21, Figure 22, Table 1, and Table 2 and in the sections above, permeation barriers can be used to reduce the effective permeation in laboratory testing [158-163, 175, 176, 178-183, 185]. The effectiveness of permeation barriers is often assessed by the PRF, which is

the ratio of the effective permeability of specimen without a barrier to an equivalent specimen with a barrier; thus the greater the PRF value, the more effective the permeation barrier. Permeation reduction factors from laboratory experiments have been reported to be many thousands in certain barrier systems [158, 163, 175, 176, 181, 182]. However, while the data available in the open literature is quite limited, there is significant evidence that the effectiveness of the permeation barriers decreases in radiation environments. There were three sets of experiments [206-209] performed in the HFR Petten reactor in the Netherlands. In the first of these experiments [206, 209] reported in 1991 and 1992, tritium was produced by the liquid breeder material Pb-17Li. Permeation of tritium through a bare 316 stainless steel layer was compared to that through an identical layer covered with a 146 μm thick aluminide coating. Over the temperature range 540 K to 760 K, the barrier was reported to decrease the permeation by a factor of 80, i.e. $\text{PRF} = 80$. In the LIBRETTO-3 experiments [207], three different permeation barrier concepts were tested with the tritium again produced by the liquid breeder material. One irradiation capsule for tritium breeding was coated on the outside with a 6 to 8 μm thick CVD layer of TiC. A second capsule was coated on the inside with a 0.5 to 1.5 μm thick layer of TiC followed by a 2 to 3 μm thick layer of Al_2O_3 . The third barrier was an aluminide coating produced by the cementation process. The aluminum rich layer was approximately 120 μm thick with about 5 μm of Al_2O_3 on the outside. The single TiC layer reduced the tritium permeation by a factor of only 3.2, the TiC and Al_2O_3 layer reduced the permeation by 3.4, and the pack cementation aluminide coating reduced the permeation by a factor of 14.7. These are surprisingly small reductions compared to laboratory experiments. In a third set of experiments [208], the tritium production was achieved with the solid ceramic breeder materials. Both double wall tubes and single wall tubes with a permeation barrier were tested. The double wall configuration had an inner layer of copper. The permeation barrier on the other system was an aluminide coating with a thickness of 7 μm . The aluminide coating was reported to be 70 more effective than the double wall configuration in suppressing permeation. Unfortunately, different breeder materials were used for the two different experiments, and the results could have been strongly affected by the amount of tritium released from the ceramic as well as the form of release (T_2 versus T_2O). The bottom line on the irradiation testing of barriers is that barriers do not appear to perform as well in a reactor environment as well as they do in the laboratory. PRF greater than 1000 simply cannot be achieved in reactors.

4.116.4.2. How Barriers Work and Why Radiation Affects Them

To understand the effects of radiation on the performance of permeation barriers, we need to first examine how barriers work. For tritium to permeate through a material with or without a coating, the tritium must absorb on the surface, dissociate into atoms, dissolve into the material, diffuse through the material, and then recombine into molecules on the downstream side. In the simple case where diffusion through the structural material is rate limiting, the permeation rate is controlled by the ratio of the permeability and the thickness of the pressure boundary (equation 16); as described above the permeability is the product of the diffusivity and the solubility, which can be thought of as the velocity times capacity. These parameters are dependent on temperature, but are not affected by radiation effects or nominal surface cracking. In the simple case of diffusion-limited permeation through the structural boundary, the experimental result determined in the laboratory can be counted on to hold in the radiation environment.

Permeation barriers, by their basic nature, consist of a thin layer adhered to the structural material. The performance of barriers depends on the integrity of the barrier as well as the

physical interaction of the barrier material with tritium. What is it about many barriers and how they operate that prevents this same agreement from being assured? In their review, Hollenberg, *et al.* [158] considered these aspects of barriers and their performance in radiation, proposing three models that describe distinct physics of the interactions between tritium and the barrier material. The most basic model is the Composite Diffusion Model, where hydrogen transport is diffusion-controlled in both the barrier and the base metal. The steady-state permeation rate (Q_∞) through a pressure boundary in this case is:

$$Q_\infty = \frac{A\sqrt{p_{TT}}}{\frac{t_B}{\Phi_B} + \frac{t_M}{\Phi_M}} ; \quad (22)$$

where A is the surface area of the boundary, and the subscripts B and M refer to the barrier and structural metal respectively. Considering the intent of the barrier, the ratio t_B/Φ_B should be much larger than t_M/Φ_M , thus the permeation is controlled simply by the permeation through the barrier.

The second model proposed by Hollenberg, *et al.* considers the barrier to be effectively impermeable to tritium and is called is the Area Defect Model. In this case, hydrogen is transported through the metal, reaching metal surface through a limited number of cracks or other defects in the barrier layer. The permeation rate for this case is:

$$Q_\infty = A_d \frac{\Phi_M}{t_{eff}} \sqrt{p_{TT}} ; \quad (23)$$

where A_d is the area of the defects and t_{eff} is the effective distance the hydrogen isotope must traverse to reach the other side of the metal.

The third model proposed by Hollenberg, *et al.* is the Surface Desorption Model, in which case permeation is controlled by the recombination rate of hydrogen isotope atoms into molecules on the back surface and the recombination-limited flux of tritium is described by equation 19. Surface desorption does not make sense by itself; as we will show below, it is actually part of the area defect model.

As reported by Hollenberg, *et al.* [158] and as revealed by a review of the literature on barriers and oxides [176, 210-212], the activation energy of permeation is generally not altered by the addition of the barrier layer onto the substrate. This means that, in practice, the permeation process itself is being controlled by the substrate, not the barrier, strongly supporting the Area Defect Model described above. The barrier works simply by limiting the area of the metal exposed to the driving pressure.

Pisarev, *et al.* [213] provide particularly intriguing insights on the effects of cracks on permeation barriers. Their report showed that permeation reduction for the Area Defect Model is difficult to achieve when the distance between defects is not larger than the combined thickness of the barrier and substrate. Inherent in this conclusion is the assumption that the dissociation rate at the defect is sufficiently fast to maintain the equilibrium concentration dictated by Sievert's law. If this condition is not met, then the activation energy for the process would be

that associated with the dissociation, and not that of permeation through the substrate. Thus, barriers that can provide a significant permeation reduction in the laboratory must be almost defect free.

The physics of hydrogen transport in metals with permeation barriers can be further understood by examining the pressure dependence of permeation. As discussed above, diffusion-controlled permeation through metals is proportional to the square root of the hydrogen partial pressure. Perujo, *et al.* [214] reported that the pressure dependence of permeation through MANET plasma sprayed with aluminum changed from the classic square root dependence to linear as the pressure was decreased below 20,000 Pa. McGuire [215] also noted the transition to near linear pressure dependence in the pressure range from 200 to 1000 Pa. Linear pressure dependence is symptomatic of permeation limited by absorption or recombination. For example, if recombination limits permeation, the concentration of hydrogen in the metal will be approximately constant and uniform, and it will be established by equilibrium at the upstream side of the pressure boundary. Thus, Sievert's Law (equation 7) can be substituted into equation 24, leading to linear pressure dependence:

$$J_r = k_r K^2 p_{TT}. \quad (24)$$

While the same relationship will be found if the permeation is limited by absorption on the upstream surface, known values for the recombination rate constant for MANET can explain the linear pressure dependence seen in permeation measurements [115]. The conclusion to be drawn is that a combination of the Area Defect Model and the Surface Desorption Model are needed to properly model permeation through barrier materials.

Now with the understanding that barriers work by limiting the area available for the gas to contact the underlying metal surface, and possibly by creating low enough permeation to have recombination even further reduce the permeation, how does radiation affect this process? The obvious answer is by increasing the porosity or cracking of the barrier. According to Arshak and Korostynska [216] properties of metal oxide materials are directly or indirectly connected to the presence of defects, oxygen vacancies in particular. Oxygen vacancies are also known as color centers, and these color centers are stabilized by hydrogen captured at the defects. The hydrogen can come from pre-existing OH⁻ groups or from small amount of hydrogen isotopes migrating through the oxide, possibly increased by the enhanced electrical conductivity generated by the radiation damage and the oxygen vacancies. While cracking was not considered by Arshak and Korostynska, one can speculate that the radiation damage with increased oxygen vacancies and trapped hydrogen would lead to a more brittle oxide layer. In metals, lateral stress from hydrogen or helium trapping can lead to blisters [217]. Without the required ductility to allow blistering, the oxide layer could experience significantly increased cracking. The cracking would then increase the area available for hydrogen to reach the metal surfaces.

4.116.4.3. Why Barriers Are Needed for Fusion Reactors

We have looked at the materials to be used in the blanket region, and described their permeation parameters. Let's look at the conditions that exist there so we can determine the need for the barriers there. As an example, let's consider the tritium migration processes that might be associated with the liquid Pb-17Li systems. In a set of experiments, Maeda, *et al.* [218] found the solubility of hydrogen in Pb-17Li to be in the range of 10^{-7} Pa^{-1/2} atom fraction. As tritium is

produced in the blanket, some of the tritium will be in solution and some will be in the vapor phase. It is the tritium in the vapor phase that will drive the permeation through the metal used to contain the liquid. For an 800 MW fusion reactor, Maeda, *et al.* state that 1.5 MCi (150 grams) of tritium will have to be bred each day. That means that 1.5 MCi of tritium will be flowing around in stainless steel or similar metal tubes at a temperature greater than 600 K. To go through a permeation calculation, we will use some of the design parameters proposed by Farabolini, *et al.* [219] for a much larger plant, but scale it back to the generic 800 MW plant mentioned above. Approximately 10,000 m² of surface area will be needed for the tubes passing through the liquid Pb-17Li to extract the heat. We will assume that a sufficient number of detritiation cycles per day are performed to keep the amount of tritium in the liquid breeder at 10% of the 150 grams listed above. Scaling to 800 MW, the amount of Pb-17Li will be approximately 750,000 kg. This leads to a molar fraction of tritium equal to 6.7×10^{-7} . Using the solubility of Maeda, *et al.* [218] for Pb-17Li yields a tritium pressure of approximately 45 Pa. Assuming the containment metal to be 1 mm of MANET with an aluminized coating, a temperature of 700 K and an effective PRF of 1000, a permeation rate of 2.7×10^{-10} T₂ mols m⁻²s⁻¹ will occur [29, 105, 109, 114, 115]. With the 10,000 m² surface area, the daily permeation rate is 0.23 moles or 1.4 grams of tritium per day. To prevent subsequent permeation through the steam generator tube walls, a tritium clean up unit will have to be applied to this helium loop. Because steam generator tube wall must be thin to permit effective heat transfer, the tritium cleanup loop will have to be extremely effective to limit release of tritium to the environment. This calculation was performed simply to show the extreme need for barriers in the blanket region of fusion reactors. Even with an active detritiation unit and a barrier providing a PRF of 1000, 1.4 grams or 14,000 curies of tritium end up in the cooling system each day. The situation is not much better for the solid breeders. The same amount of tritium will obviously be required for that system. To minimize the tritium hold up in the ceramic breeder materials (to minimize inventory), temperatures equal to or greater than that for the liquid breeder will be maintained. With the fractional forms depending on the type of ceramic breeder used, the tritium will be released into the helium coolant as elemental tritium (T₂) and tritiated water (T₂O). The steel or similar containment metal will be exposed to non-trivial pressures of tritium gas. The conclusion to be drawn is that effective barriers are needed for the blanket. It is difficult to imagine that even with double walled designs that fusion reactor facilities can meet radioactive release requirements for tritium without an effective barrier.

4.116.5. SUMMARY

In this chapter, we have presented tritium permeation characteristics and parameters for materials used in fusion reactors. These materials have included those used to face the plasma in the main chamber as well as materials used as structural materials for the main chamber and blanket. A description of the conditions that exist in those locations has also been provided. Reasons were given why direct contact of the plasma with the plasma facing materials would not lead to sizeable quantities of tritium being lost to the environment or to the cooling system. The same was not concluded for the blanket region. The need for permeation barriers there was stressed. A number of materials were listed as possible tritium barriers. These materials included a few metals with somewhat reduced permeation and a larger number of ceramics with very low tritium permeability. Due to the difficulty of lining large chambers with bulk ceramics, much of the tritium permeation barrier development around the world has been dedicated to thin ceramic layers on metal surfaces. Unfortunately, radiation testing of these materials has shown these thin layers to lose their ability to limit tritium permeation during exposure to radiation damage. It was suggested, but not proven, that this increase in permeation was due to cracking of the ceramics or the general increase in defects.

To make this chapter more useful to the reader with a need for permeation data, tables and plots of the permeation coefficients are provided. The coefficients for metals are presented in Table 1 and Figure 21 and for the ceramics in Table 2 and Figure 22. The actual parameters used to produce these figures are taken from the individual sections of the chapter.

In summary, effective permeation barriers are needed for fusion reactors to prevent the release of sizeable quantities of tritium. Fusion is touted as a clean form of energy, and releasing tritium into the environment will eliminate any political advantage that fusion has over fission. Research is needed to find ways to place radiation resistant ceramic permeation barriers on top of structural metals. The fusion community must find a way to make this happen.

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Table 1. Recommended diffusivity and solubility relationships for protium in various metals and classes of alloys in the absence of trapping.

Alloy	Diffusivity $D = D_o \exp(-E_D / RT)$		Solubility, Φ/D $K = K_o \exp(-\Delta H_s / RT)$		Ref.
	D_o	E_D	K_o	ΔH_s	
	$\left(\frac{\text{m}^2}{\text{s}}\right)$	$\left(\frac{\text{kJ}}{\text{mol}}\right)$	$\left(\frac{\text{mol H}_2}{\text{m}^3 \cdot \sqrt{\text{MPa}}}\right)$	$\left(\frac{\text{kJ}}{\text{mol}}\right)$	
Beryllium	3×10^{-11}	18.3	18.9 * $5.9 \times 10^6 *$	16.8 * 96.6 *	[73] [43] [78]
Graphite	9×10^{-5}	270	19	-19.2	[43]
Aluminum	2×10^{-8}	16	46	39.7	[220] [150]
Vanadium	$3 \times 10^{-8} \dagger$	4.3 †	138	-29	[127] [197]
RAFM steels ‡	1×10^{-7}	13.2	436	28.6	
Austenitic stainless steel	2×10^{-7}	49.3	266	6.9	[95]
Nickel	7×10^{-7}	39.5	564	15.8	[153]
Copper	1×10^{-6}	38.5	792	38.9	[154]
Zirconium	8×10^{-7}	45.3	3.4×10^7	35.8	[143] [221]
Molybdenum	4×10^{-8}	22.3	3300	37.4	[198]
Silver	9×10^{-7}	30.1	258	56.7	[199] [200]
Tungsten	6×10^{-4}	103.1	1490	100.8	[53]
Platinum	6×10^{-7}	24.7	207	46.0	[202]
Gold	5.6×10^{-8}	23.6	77900 §	99.4 §	[205]

* per the text, the solubility of hydrogen in beryllium is very low and there is not good agreement between the few studies of the material

† data for isotopes other than protium does not scale as the square root of mass

‡ values are averaged over the data presented in Figure 12 and Figure 13

§ estimated using the permeability from Ref. [203] and the quoted diffusivity.

Table 2. Recommended diffusivity and solubility relationships for protium in various non-metallic materials in the absence of trapping.

Material	Diffusivity $D = D_o \exp(-E_D / RT)$		Solubility, Φ/D $K = K_o \exp(-\Delta H_s / RT)$		Ref.
	$\left(\frac{D_o}{\text{m}^2/\text{s}}\right)$	$\left(\frac{E_D}{\text{kJ/mol}}\right)$	$\left(\frac{K_o}{\text{mol H}_2 / \text{m}^3 \cdot \sqrt{\text{MPa}}}\right)$	$\left(\frac{\Delta H_s}{\text{kJ/mol}}\right)$	
Al ₂ O ₃	1.1x10 ⁻⁸	132	5.5	22.5	[165] [222]
α -ZrO ₂	4x10 ⁻¹⁸	30.1	2.5x10 ⁻²	-28.2	[141] [139]
UO ₂	3.7x10 ⁻⁶	59.8	9.6x10 ⁴	100	[223]
BC	1.2x10 ⁻¹¹	80.8	3.8	-29.8	[186]
SiC	9.8x10 ⁻⁸	182	2.2x10 ⁻²	-58.7	[191]

Figure 1. Fraction of filled traps as a function of temperature for “low-solubility” and “high-solubility” materials (modeled as RAFM steel and austenitic stainless steel respectively using relationships from Table 1). The pressure is 0.1 MPa, the molar volume of the steels is approximated as $7 \text{ cm}^3 \text{ mol}^{-1}$ and there is assumed to be one lattice site for hydrogen per metal atom.

Figure 2. Ratio of effective diffusivity to lattice diffusivity (D_{eff}/D) as a function of temperature for “low-solubility” material (squares with varying n_T , modeled as RAFM steel with $E_t = 50 \text{ kJ mol}^{-1}$) and “high-solubility” material (triangles, modeled as austenitic stainless steel with $E_t = 10 \text{ kJ mol}^{-1}$ and $n_T = 10^{-3}$ traps per metal atom). The pressure is 0.1 MPa, the molar volume of the steels is approximated as $7 \text{ cm}^3 \text{ mol}^{-1}$ and there is assumed to be one lattice site for hydrogen per metal atom.

Figure 3. Solubility of hydrogen in carbon [43, 44].

Figure 4. Diffusivity of hydrogen in graphite [43-47]. The bold line is the best estimate given in Ref. [44] based on uptake data for tritium in POCO AFX-5Q graphite.

Figure 5. Diffusivity of hydrogen in W [53-55].

Figure 6. Solubility of hydrogen in W [53, 56].

Figure 7. Recombination rate coefficient of hydrogen in W [24, 62].

Figure 8. Diffusivity of hydrogen in Be [72-74].

Figure 9. Solubility of hydrogen in Be [73, 77, 78].

Figure 10. Diffusivity of hydrogen in austenitic stainless steels from gas permeation studies that confirmed diffusion-limited transport [5, 92, 93, 95, 98, 102, 103, 224, 225]. The bold line represents the average relationship determined in Ref. [95] for several austenitic stainless steels.

Figure 11. Solubility of hydrogen in austenitic stainless steels from gas permeation studies that confirmed diffusion-limited transport [5, 92, 93, 95, 98, 102, 103, 224, 225]. The bold line represents the average relationship determined in Ref. [95] for several austenitic stainless steels.

Figure 12. Diffusivity of hydrogen in RAFM steels from gas permeation studies that confirmed diffusion-limited transport [7, 19, 105, 106, 108, 226, 227]. The bold line represents an approximate relationship estimated from the plotted data.

Figure 13. Solubility of hydrogen in RAFM steels from gas permeation studies that confirmed diffusion-limited transport [7, 19, 105, 106, 108, 226, 227]. The bold line represents an approximate relationship estimated from the plotted data.

Figure 14. Diffusivity of hydrogen in V and its alloys [118-129, 133, 134, 228-230]. The bold line represents the relationship for pure V, reported in Ref. [127].

Figure 15. Solubility of hydrogen in V and its alloys [123, 197, 230-233]. The bold line represents the relationship for pure V, reported in Ref. [197].

Figure 16. Solubility of hydrogen in Zr and its alloys [144, 221, 234-240]. The bold line represents the average for thirteen studies on pure Zr and Zr-based alloys, reported in Ref. [221].

Figure 17. Diffusivity of hydrogen in Zr and its alloys [140-145, 149, 241, 242]. The bold line represents the relationship for pure Zr, reported in Ref. [143].

Figure 18. Diffusivity of hydrogen in alumina [165, 222, 243]. The bold line represents the average for many aluminas, reported in Ref. [165].

Figure 19. Solubility of hydrogen in alumina [164, 222].

Figure 20. Permeability of hydrogen in SiC [191-193].

Figure 21. Permeability of hydrogen in various metals using data from Table 1 [53, 95, 127, 143, 150, 153, 154, 197-200, 202, 205, 220, 221]. Data is distributed across two separate plots for clarity.

Figure 22. Permeability of hydrogen in various ceramics using data from Table 2 [139, 141, 165, 186, 191, 222, 223].

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