SURFACE EFFECTS ON TRITIUM DIFFUSION
IN MATERIALS IN A RADIATION ENVIRONMENT

by

G. R. Caskey, Jr.

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Proposed for presentation at the
170th National Meeting of the American Chemical Society
Chicago, Illinois
August 25-26, 1975;

and for publication in
Advances in Chemistry
as part of the
"Symposium on Radiation Effects on Solid Surfaces."

Mail to:

Dr. M. Kaminsky
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60440

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Energy Research and Development Administration. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copy-right covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copy-righted paper.

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SURFACE EFFECTS ON TRITIUM DIFFUSION
IN MATERIALS IN A RADIATION ENVIRONMENT

G. R. Caskey, Jr.

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina

ABSTRACT — Tritium transport and distribution in a material are controlled by chemical potential and thermal gradients and cross-coupling to impurities and defects. Surfaces influence tritium diffusion by acting as sources and sinks for defects and impurities, and surface films restricting tritium transfer between the solid and surrounding fluids. Radiation directly affects boundary processes such as dissociation or adsorption, may erode a surface film or the surface itself, and introduces defects and impurities into the solid by radiation damage, transmutation, or ion implantation, thereby modifying tritium transport within the solid and its transfer across external interfaces. There have been no definitive investigations of these effects, but their practical significance has been demonstrated in tritium release or absorption studies with stainless steel, Zircaloy, niobium, and other materials.

INTRODUCTION

Current interest in tritium migration in solids arises from technical, economic, and environmental considerations associated with operating fission reactor plants and projected fusion reactor systems. In the first case, the interest is almost entirely due to the possible environmental contamination by tritium leakage to plant effluents (1,2). Small quantities of tritium are generated by both ternary fission and reaction of neutrons with boron and lithium. This tritium may eventually escape to the environment along several paths; for example, permeation through the steam generator system. Fusion reactors, on the other hand, are designed to process continuously large (kilogram) quantities of tritium both in the feed and exhaust from the deuterium-tritium (D-T) plasma and in the tritium breeding, extraction, and purification systems (3-7). Efficient containment and recovery are essential in this case. Potential problems associated with fusion systems have been described in detail (4-6), and several alternative approaches to minimize tritium release have been advanced (4). In all cases, knowledge of the diffusion and permeation characteristics of tritium in structural materials of principal interest is helpful in analyzing containment, breeding, and handling problems. Potential materials include: stainless steel, niobium, vanadium, molybdenum, and Zircaloy-2; silicon carbide, beryllium oxide, and alumina; oxides commonly formed as surface films on metals; and tritides, such as TiT_2 which may be used in targets

for neutron generation (8) and in extraction systems. A small amount of experimental data is available on tritium diffusion in these materials. There is a much larger body of information for protium and deuterium (9-12) which is applicable to tritium, if the data are corrected for the effects of isotope mass.

Tritium diffusion occurs in response to gradients in chemical potential and temperature in solids and is influenced by interaction with defects, impurities, and with surfaces. These interactions may involve:

- Boundary processes such as dissociation and chemisorption.
- External surfaces (such as those between two solids or between a solid and a fluid) and internal surfaces (such as grain boundaries) which act as sources and sinks for defects and impurities.
- Surface films, such as oxides on metal surfaces, which may slow tritium transfer between phases.

Potential interrelations among these factors are represented diagrammatically in Figure 1, which also indicates several possible effects of radiation on the processes affecting tritium diffusion, including:

- Catalytic effect on dissociation or adsorption.
- Erosion of the surface or of surface films.
- Increased defect and impurity fluxes to or from the surfaces.
- Increased defect and impurity concentrations within the solid.

The effects of these processes on tritium diffusion in solids

have not been investigated. Several related problems, however, have been discussed or are under investigation (13). For example, the effect of oxide films on tritium release and permeation in stainless steel (14), trapping effects in niobium (11), and photo-desorption (15,16) have all been reported in some detail. The present discussion will focus attention on those aspects of tritium absorption and transport where information is available and where experimental investigation is in progress. An attempt will also be made to identify areas where additional investigation is needed.

INTERACTION BETWEEN SURFACES AND DEFECTS OR IMPURITIES

Tritium diffusion and its ultimate distribution throughout a solid is strongly affected by the presence of lattice defects and impurities because of repulsive or attractive interactions. Such interactions include:

- Trapping of tritium at immobile defects or impurities.
- Diffusion of tritium in response to gradients in the chemical potential of impurities.
- Migration of tritium with moving defects.

These processes are related to radiation effects because radiation damage, transmutation, and ion bombardment change the number and distribution of defects and impurities and may implant tritium within the lattice.

Tritium Solution in Solids

Dissolved tritium may occupy either octahedral (O) or tetrahedral (T) interstitial positions in metals depending on the crystal lattice of the host structure. Neutron diffraction, ion-channeling, and nuclear magnetic resonance techniques have identified the equilibrium interstitial sites in several metals (17-20). Generally, the T-site is occupied in metals with a body-centered-cubic (BCC) lattice and the O-site is occupied in metals with a face-centered-cubic (FCC) or hexagonal-close-packed (HCP) lattice. Chromium (BCC) appears to be an exception, as an ion-channeling study indicates that the O-site is occupied (21).

Atomic and molecular solutions of tritium have been observed in nonmetallic solids (22-29), but there is very limited direct evidence about the specific location of tritium in such materials. Generally, interstitial solution is assumed, although substitutional replacement may be anticipated in some cases, as polymers. Tritium solution and diffusion in silica and silicate glasses is normally molecular (22,23); however, atomic diffusion of tritium ions has been observed in quartz and fused silica (24), and electrolysis apparently introduces atomic hydrogen in vitreous silica (25). Tritium solution in polymers is normally molecular as indicated by the direct dependence of permeation rate on the first power of the hydrogen pressure (26). In this instance, isotopic exchange of tritium with the hydrogen in the polymer could alter the diffusion kinetics and eventually degrade the

polymer by breaking the bonds where replacement tritium decayed. Tritium solution in metal oxides is believed to be atomic in the few cases where it has been studied, e.g., ZnO (27) and TiO₂ (28); however, the pressure dependence of the permeation rate of hydrogen in ZrO₂ suggests a molecular solution (29).

Tritium diffusivity has been measured in a variety of materials by gas phase charging (28), electrolytic charging (25), ion bombardment (24), and recoil from transmutation of ⁶Li (14). Results for several types of solid are shown in Figure 2. Generally, tritium diffusivities correlate with protium or deuterium diffusivities by the inverse-square-root-of mass relation where data exist to make the comparison. Silver and aluminum are apparent exceptions, because of effects associated with ion implantation or radiation, as discussed later. Protium and deuterium diffusivities in metals have been summarized previously (9-12). Little work has been done with oxides, but this area of investigation is being pursued currently on materials of interest in fusion reactor development (30).

Trapping by Immobile Defects or Impurities

An attractive interaction between diffusing tritium and lattice defects or impurity atoms is not accounted for in the simple diffusion equation, $\partial C/\partial t = \nabla D \nabla C$. Therefore, this equation is not applicable under such conditions. More complex formulations are required to incorporate additional processes into the analysis. Formal representation of trapping has been approached in two ways; incorporation of additional terms in the continuum diffusion

equation to account for trapping (31-35), and analysis based on the concept of mean-free passage time taken from the theory of stochastic processes (36). The former approach has been used extensively, but may not be appropriate when considering singularities of atomic dimension. The latter approach takes into account details of the lattice, trap site, and shifting of the saddle point energy due to the perturbation of the lattice by the defect, but has not been applied to analysis of hydrogen diffusion experiments.

Trapping sites that have been identified or suspected in metals include: dislocations in Type 304L stainless steel, nickel, vanadium, niobium, iron, and molybdenum (37-42); interstitial or vacancy clusters in copper, silver, and gold (43); oxygen in niobium and copper (44,45); and voids or gas bubbles in iron, silver-lithium, and aluminum-lithium alloys (46-48). Potential trapping sites in nonmetallic solids include Schottky or Frenkel defects and impurity atoms.

General representation of diffusion with trapping at only one type trap has been developed (33) by replacing the simple differential equation with $\partial C/\partial t + N\partial n/\partial t = D\nabla^2 C$, where: $\partial n/\partial t = kC(1-n) + pn$, N is the number of traps per unit volume, n is the fractional occupancy of trap sites, and k and p are capture and release probabilities. The resulting equations are nonlinear and have no general analytic solution. Finite difference methods have been applied to yield approximate solutions for boundary and

initial conditions corresponding to permeation and evolution from a plane sheet (49). Exact solutions have been obtained for certain limiting cases where the equation reduces to a linear form (33, 34,50). Characteristics of trapping effects on permeation and evolution (Table 1) show that: apparent diffusivity is less than the true lattice diffusivity; actual solubility is greater than the lattice solubility; and steady-state processes are unaffected.

The temperature dependence of apparent diffusivity may not be simple because of interrelationships between the temperature dependencies of C , D , N , k , and p . Basically, expectation and available experimental data indicate that trapping should be more pronounced at lower temperatures. This implies that trapping will not be significant in the first wall of a fusion reactor, but may be important in the colder portions, such as the tritium recovery and extraction systems. Trapping may also be important in assessing release from fuel element cladding in fission reactors.

Internal Surfaces

Internal surfaces, such as grain and subgrain boundaries, may serve as trap sites or act as short-circuit diffusion paths. For example, hydrogen solubility in polycrystalline nickel is distinctly greater than in single crystals over a wide temperature range. Further, the solubility in polycrystalline nickel deviates increasingly from the expected temperature dependence as the temperature is lowered below 700°K (51). Trapping effects are also observed in tritium solubility measurements for cold-worked and annealed nickel (52) between 300 and 500°K (Figure 3).

Tritium has been introduced into silver and aluminum by ion bombardment (47) and its diffusivity calculated from release rate measurements. The release rates were slower than expected from calculations based on gas phase charging and evolution measurements. This lowering of apparent diffusivity was attributed to the formation of bubbles of tritium. The bubbles were assumed to form at accumulations of point defects or dislocation loops generated during ion bombardment when the lattice is supersaturated with tritium. Release rates were, therefore, controlled by bubble migration at low temperatures or re-solution and diffusion at higher temperatures. As shown in Figure 2, apparent tritium diffusivities calculated by this technique are very much lower than for other metals or alloys and are less than calculated from hydrogen diffusivity data (53).

Neutron irradiation of Ag-Li and Al-Li alloys generates tritium by an (n,α) reaction (48,54). Autoradiographic examination of the aluminum alloys containing 0.4 to 2.7 wt% lithium revealed gas bubbles along grain boundaries (54). These bubbles presumably contained both tritium and helium. Annealing of the irradiated samples apparently led to bubble agglomeration (54). After annealing at relatively high temperatures (i.e., 625°C), the Al-2.7 wt% Li alloy was free of bubbles because all the tritium and helium were released during the anneal. The outgassing behavior of the silver alloy showed nonideal diffusion characteristics between 280 and 600°C (48). This nonideal

diffusion was attributed to trapping of the tritium at point defect clusters and is similar to the results from ion bombardment (47).

Tritium-Dislocation Interaction

A considerable body of information on the interaction of hydrogen with lattice defects in metals and alloys has been accumulated. The prototypical case is that of α -iron where substantial deviation between the anticipated and measured temperature dependence of the diffusivity is observed at lower temperatures (Figure 4). In this case, the extent of cold work, and hence the dislocation density, substructure, and microvoid formation, appear to play major roles in affecting the measured diffusivity. Steady-state permeation rates are unaffected (Reference 55 and Figure 5).

The behavior exhibited by iron, however, is not unique. Similar features are observed in gold, where the diffusivity differences correlate with heat treatment and are attributed to vacancies, vacancy clusters, or stacking-fault tetrahedra (53). Platinum (53), silver (53), copper (53), nickel (52), molybdenum (56), vanadium (13), and niobium (10), are also known to exhibit similar behavior. This behavior is also not unique to dislocation trapping, but occurs with any reversible trap.

Evidence for trapping of hydrogen at dislocations in the refractory metals has been derived from mechanical tests. Variations in the yield points of molybdenum wires saturated with hydrogen

at high temperature and then quenched were attributed to hydrogen segregation at dislocations (37). Recent deuterium permeation studies and autoradiographic examination of molybdenum wire saturated with tritium at 428°K provided further evidence of trapping but did not identify the trapping site (56). Yield point behavior following hydrogen charging has been taken as evidence of a hydrogen-dislocation interaction in vanadium (38), niobium (39), and nickel (57).

Both external and internal surfaces can act as sources or sinks for dislocations (40). During plastic deformation, a dislocation may move inwardly from the external surface dragging tritium atoms which were picked up at the surface. This has been reported for Type 304L stainless steel tensile specimens tested in 69-MPa tritium. Concentration of tritium along slip planes was also observed in the autoradiographs. A free surface is also a dislocation sink; therefore, tritium may be pulled out of the interior of a metal and rejected to the surrounding atmosphere during plastic deformation. Tritium release from iron, Type 304L stainless steel, *Inconel** 718, nickel, and 5086 aluminum correlated with plastic deformation (40).

Temperature is a particularly important parameter in the deformation-enhanced tritium transport phenomenon. Both the binding of the tritium to the dislocation and the ability of the

* Registered trade name of the International Nickel Company, Huntington, West Virginia.

tritium to diffuse with the moving dislocation are temperature dependent. At a high temperature, binding is weak, and little transport occurs because of the small tritium atmosphere; at low temperatures, tritium movement is restricted, and the dislocations break away from the tritium atmosphere and, again, little transport occurs. Practical effects of dislocation transport are restricted, therefore, to an intermediate temperature range.

Effects of Impurity Fluxes

Interstitial diffusion of tritium is generally considered in terms of gradients in the chemical potential of tritium and temperature gradients (Soret effect). However, a diffusive flux may also develop in response to gradients in chemical potential of other independent species in solution. The phenomenological equations of irreversible thermodynamics provide general relations among the thermodynamic forces and the conjugate fluxes (59).

The special case of isothermal diffusion of one interstitial and one substitutional solute illustrates the nature of the cross effects (60). The interstitial (J_1) and substitutional (J_2) fluxes are related to the concentration gradients, ΔC_1 and ΔC_2 , through the diffusion coefficients, D_{ij} :

$$J_1 = - D_{11} \nabla C_1 - D_{12} \nabla C_2 \quad (1)$$

$$J_2 = - D_{21} \nabla C_1 - D_{22} \nabla C_2 \quad (2)$$

For the assumptions made in the derivation, the ratios of the diffusion coefficients in the volume fixed frame of reference were found to be:

$$\frac{D_{12}}{D_{11}} = X_1 \epsilon_{12} - \left(\frac{X_1^2}{(L_{11})_k X_2} \right) \left((L_{22})_k - X_2 (L_{33})_k \right) \quad (3)$$

and

$$\frac{D_{21}}{D_{22}} = X_2 \epsilon_{21} + X_2^2 \left[\frac{(L_{33})_k}{(L_{22})_k} \right] \quad (4)$$

In Equation 3, X_i is the mole fraction of i , $(L_{ii})_k$ are coefficients in the Kirkendall frame of reference, and the interaction coefficients ϵ_{ij} are from the Taylor expansion of the activity coefficients γ_i in the mole fraction:

$$\ln \gamma_i = \ln \gamma_i^0 + \epsilon_{ii} X_i + \epsilon_{ij} X_j \quad (5)$$

The initial terms in the expression for the ratio of diffusion coefficients are of purely thermodynamic origin; the second terms are kinetic.

The ratios D_{12}/D_{11} and D_{21}/D_{22} cannot be calculated without the necessary thermodynamic and kinetic data. However, their magnitudes may be roughly estimated. This will permit the assessment of the relative contribution of the cross terms to tritium diffusion in dilute solution. The thermodynamic terms, $X_1 \epsilon_{12}$ and $X_2 \epsilon_{21}$, will be less than 1 for dilute solutions because X_1 and $X_2 \ll 1.0$, and interaction parameters are estimated to lie in the range -5 to +5 based on experimental determination of alloying effects on hydrogen solution in liquid iron and cobalt (100,103).

Estimates of the kinetic terms indicate that they may be small also. In both expressions, ratios of L's occur, which are expected to be of about 1. Of more importance, however, is the fact that these ratios are multiplied by a mole fraction ($\ll 1.0$) or its square, except for the term $[X_1^2/(L_{11})_k^2]/(L_{22})_2$ where the ratio X_1^2/X_2 could easily vary from 10^2 to 10^{-2} depending on the concentrations.

This type of analysis indicates that the contributions of $D_{12}\nabla C_2$ and $D_{21}\nabla C_1$ to the fluxes J_1 and J_2 are expected to be smaller than the direct diffusion effects. The contribution need not be insignificant, however, since the gradients may be relatively large under prevailing conditions in fission or fusion reactors. Further investigation of the cross effects is clearly needed to evaluate their possible contribution to tritium diffusion.

EXTERNAL SURFACE FILMS

Oxides are probably the most common form of surface film on metals and are also observed on nonmetallic materials which are readily oxidized, for example, silicon. Surface oxidation is seldom purposely avoided in handling laboratory specimens and is clearly not controlled during the fabrication of large engineering structures. Furthermore, operating conditions may often lead to formation or growth of oxide films, even when they were absent initially. Presence of an oxide film may influence tritium transport in several ways:

- Oxides usually have a lower permeability than the base materials and thus restrict tritium uptake and release.
- Oxide-metal interfaces act as sources and sinks for vacancies and oxygen atoms during growth or reduction of an oxide film.

The extent to which tritium transport is affected by an oxide film will depend on the stability of the oxide in the ambient environment, its thickness, its permeability relative to the substrate, and its structural continuity and perfection. Anomalies in permeation behavior of *Inconel** (63). *Incoloy** 800 (64), Type 304 stainless steel (65,66), and niobium (67) have been observed and attributed to oxide films formed prior to exposure to hydrogen.

Stability of Oxide Films

The thermodynamic stability of an oxide on a pure substance may be evaluated from available thermochemical data on dissociation pressure and for possible reactions with species in the surrounding environment that may contact the surface (68). For example, oxide reduction by hydrogen gas may occur:

Possible reactions between oxides of chromium, niobium, iron, and molybdenum with hydrogen gas are readily evaluated by this equation, and are illustrated in Figure 6.

* Registered trade names of the International Nickel Company, Huntington, West Virginia.

The stability of oxides on commercial alloys is more difficult to assess, since the composition of the oxide may vary widely depending on the circumstances surrounding its formation. On stainless steel, for example, the oxide may be nearly pure Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ spinel, $\text{MnO}\cdot\text{Cr}_2\text{O}_3$ spinel, or one of the iron oxides (64,68,69). Cr_2O_3 is relatively stable in hydrogen, whereas the iron oxides may be reduced unless the oxygen potential of the gas phase is relatively high.

Aluminum alloys are interesting, because several oxides of the general form $\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$ may form where n is 0, 1, 2, or 3. The hydrated oxides readily form in the presence of relatively low water vapor pressures and are more stable in hydrogen than the pure $\alpha\text{Al}_2\text{O}_3$ (corundum).

Effects of Oxide Films

Few experimental data exist on diffusivity or permeability of tritium (or any hydrogen isotope) in oxides which normally form as surface films on materials. Where data are available, tritium diffusivity and permeability for the oxide are observed to be lower than for the base material. This is shown for tritium diffusivity in silicon and silicon dioxide in Figure 2. Tritium diffusivity in aluminum oxide and titanium dioxide (53) is also lower than in the corresponding metals. Experiments with oxidized zirconium, niobium, stainless steel (66,70,71), and titanium (72), conform to the expectation of a lower release, absorption, or permeation rate than with "clean" metal surfaces.

Tritium evolution from Type 304 stainless steel, Zircaloy-2 and niobium has been analyzed successfully by assuming an oxide-metal laminate (71). The oxide films were assumed to be continuous and free of high diffusivity paths. The surface of the Type 304 stainless steel specimen had an apparent diffusivity of about 10^{-15} cm²/sec, a value comparable to results on Type 302 and Type 347 stainless steels obtained from hydrogen evolution following cathodic charging (73). In both cases, the boundary conditions at the oxide-metal interface are: $D_o \partial C_o / \partial x = D_m \partial C_m / \partial x$, and $C_o = C_m$. This last condition is not true in general and should be replaced by $C_o / C_m = k$, where the distribution coefficient (k) accounts for differences in the activity coefficients of tritium in the two phases (74). The necessary thermodynamic data are lacking, however, so the simpler condition ($C_o = C_m$) may be taken as an expedient approximation until solubility studies on oxides have been made.

Hydrogen pickup by titanium and its alloys is delayed very effectively by the naturally occurring oxide films (72). Experiments on the hydriding of Ti-5Al-2½Sn alloy at low temperatures have been rationalized with a model that represents the oxide film thickness (δ) and diffusivity (D_o) as a film coefficient ($h = D_o / \delta$) in the relation $D_m \nabla C_m = h(C_s - C)$, where C_s is the surface concentration of hydrogen in the metal at saturation. In this instance, tritium diffusivity in pure rutile (TiO₂) single crystals was known (28). The oxide film thickness was not measured, but was estimated from available studies (75) on

oxidation of titanium. Further, the large anisotropy in diffusivity observed in TiO_2 is a characteristic that may be anticipated in other oxides with noncubic lattices. This factor could be significant in determining the overall permeation rate through highly textured metals where oxide film growth is epitaxial.

Perfection of an oxide film on a metal base is questionable in light of the available information on the morphology of growing oxides (76). Film formation apparently begins by the nucleation of isolated islands which then grow together. Presumably, this growth pattern could lead to the presence of high diffusivity paths along the oxide grain boundaries. Permeation through stainless steel at low pressures has been analyzed by assuming an impermeable oxide with a small area of pores (70). The model predicts defect-controlled permeation at low pressures, and either oxide- or metal-controlled permeation at higher pressures. The apparent thickness dependence of hydrogen diffusivity in oxides on Type 302 and Type 347 stainless steel alloys may be a result of changes in film perfection with oxide film thickness (73).

Formation of an oxide film is often accompanied by some solution of oxygen in the metal. Since oxygen dissolves interstitially in many metals (76), for example, α -titanium, α -zirconium, niobium, and vanadium, an enhanced or diminished tritium concentration could occur from attractive or repulsive oxygen-hydrogen interaction. The only reported observation of this effect is a study of the Ti-O-H ternary, that demonstrates that the hydrogen

concentration is lowered as oxygen concentration increases for a fixed hydrogen potential (77).

Effects Associated with Unstable Films

Removal or growth of an oxide film during tritium transport may be expected to influence diffusion in one of several ways:

- Interaction between the interstitial tritium and the vacancy flux caused by changes on oxide thickness.
- Interaction between the interstitial tritium and oxygen flux in the metal lattice.
- Change of the chemical potential of tritium at the substrate surface upon addition or removal of an oxide film.

Whereas removal of an oxide film may occur by several processes, such as erosion, reduction by tritium gas, dissociation, or chemical reaction, growth of an oxide is restricted by requiring an adequate oxygen potential in the environment at the interface.

Oxide films may grow by cation diffusion in the substrate to the oxide interface or by anion diffusion through the oxide the interface (78-80). In both instances, there will be a vacancy flux in the substrate. Vacancies are generated at the interface and diffuse into the substrate, or vacancies in the substrate diffuse to the interface, respectively. Furthermore, vacancy absorption by the substrate may lead to void formation along grain boundaries or at the substrate-oxide interface.

Tritium migrates by interstitial diffusion, but a vacancy flux in the metal lattice could interact with diffusing tritium in the same manner as discussed for an impurity flux. Also, the

presence of excess vacancies in the metal lattice (or vacancy clusters) could serve as trapping sites leading to a higher-than-normal accumulation of tritium near the surface and a lower apparent diffusivity. High concentrations of tritium in the near-surface regions have been observed in copper (Figure 7), as well as in silicon (81), stainless steel, zirconium, and niobium (71). Interpretation is not unequivocal, however, and a high surface concentration of tritium could be attributed to interaction with dissolved oxygen or with an oxide film directly, rather than an accumulation of vacancies with associated tritium atmospheres.

Reaction between surface oxide films and hydrogen has been observed in permeation experiments. Apparatus constructed of Type 304 stainless steel has been shown to be reactive with deuterium gas at elevated temperatures to produce water vapor which is then available for reaction with other surfaces (82). Thus, oxygen could be transferred from the oxide film on stainless steel to a more reactive metal such as niobium. Oxidation of the niobium would alter its permeability to hydrogen or increase trapping effects (83).

Hydrogen evolving into a vacuum through an oxidized metal surface has been shown to react with the oxygen on the exit surface to form water vapor (84). This phenomenon directly affects a permeation measurement, especially at low hydrogen pressures, because all of the evolving hydrogen may not be accounted for unless the water vapor is measured and this hydrogen is included in

the total quantity evolved. In a fusion reactor, tritium diffusing through a first wall of stainless steel into the vacuum would be partly converted to T_2O before entering the plasma exhaust. This would require reduction to T_2 before returning to the plasma feed.

BOUNDARY PROCESSES

The importance of boundary processes, such as dissociation and adsorption, or dissolution of tritium in a solid and its subsequent diffusion is attested to by numerous observations. Carbon dioxide, carbon monoxide, and sulfur dioxide, for example, poison the surface of iron preventing or hindering hydrogen solution (85). Consequently, radiation might be expected to influence tritium diffusion in a solid either by directly affecting adsorption, desorption, or dissociation, or by removing in some manner adsorbed species that might interfere with tritium across the surface. Boundary processes are the mechanism by which the surface concentration of tritium in a solid is established and, therefore, they directly affect diffusion. In terms of the formal mathematical description, the boundary processes establish the boundary conditions required for solution of the diffusion equations. Electron- and photon-induced desorption and sputtering are radiation effects that will directly affect the boundary processes. These have been discussed earlier in this Symposium and will not be covered further.

SUMMARY

A number of ways have been identified by which an external or internal surface may affect tritium diffusion in solid materials.

These include:

- Growth or reduction of surface oxide films may generate a flux of vacancies, oxygen, or metal atoms in the bulk metal, altering tritium diffusion.
- Boundary processes (e.g., dissociation, adsorption, or solution) may directly control the transfer rate of tritium across an interface, thus affecting bulk diffusion.
- Surfaces, acting as sources and sinks for defects and impurities, may interact with diffusing tritium, also affecting bulk diffusion.

The several surface effects may in turn be altered by radiation, thus modifying whatever influence the surface may have had on the bulk diffusion of tritium. The principal effects of radiation are to alter the rates of surface processes and to introduce defects and impurities into the solid. Data to provide an assessment of the extent to which the radiation effects do in fact modify tritium diffusion are not available; however, such an assessment must be made before details for tritium transport in a radiation field can be developed.

Several topics of both academic and practical interest are suggested for further investigation including:

- Pressure and temperature dependence of tritium solubility in oxides, and the influence of defect structures and the Fermi energy in the oxide on the tritium solubility.

- Thermodynamics of metal - oxygen - hydrogen ternary systems and the possible altered hydrogen solubility in the near-surface regions when oxide films are present.
- Tritium flux in the presence of gradients or fluxes of vacancies or other impurities in a material.
- Direct measurements of the effects of irradiation on transient and steady-state tritium permeation through materials.

REFERENCES

- (1) AEC (1973), USAEC Report WASH-1250.
- (2) E. L. Compere, S. H. Freid, and C. W. Nestor (1974), USAEC Report ORNL-TM-4303.
- (3) R. G. Hickman (1973), USAEC Report UCRL-74633.
- (4) J. E. Draley, R. A. Krakowski, T. A. Coultas, and V. A. Maroni (1975), USAEC Report ANL-8019.
- (5) L. A. Booth (1973), *Nucl. Eng. Design* 24, 263.
- (6) A. H. Spano and A. Belozarov (1974), *Nucl. Fusion* 14, 281.
- (7) R. C. Forrester, III and J. S. Watson (1974), *Nucl. Fusion* 14, 281.
- (8) R. A. Nickerson (1975), USAEC Report UCRL-51737.
- (9) R. E. Stickner (1972), in *The Chemistry of Fusion Technology*, Plenum Press, New York.
- (10) J. Voekl and G. Alefeld (1975), in *Diffusion in Solids*, Academic Press, New York.
- (11) H. K. Birnbaum and C. A. Wert (1972), *Ber. Bunsen-Besell. Phys-Chem.* 76, 806.
- (12) W. G. Perkins (1973), *J. Vac. Sci. Technol.* 10, 543.
- (13) V. A. Maroni (1975), *J. Nucl. Mater.* 53, 293.
- (14) T. S. Elleman and K. Verghese (1975), *J. Nucl. Mater.* 53, 299.
- (15) D. Lichtman (1975), presented at this symposium.
- (16) S. Brumback and M. Kaminsky (1975), presented at this symposium.

- (17) E. O. Woolan, J. W. Cable, and W. C. Koehler (1963), *J. Phys. Chem. Solids* 24, 1141.
- (18) K. Skold and G. Nelin (1967), *J. Phys. Chem. Solids* 28, 236.
- (19) H. D. Carstanjen and R. Sizmann (1972), *Ber. Bunsengn.* 76, 1223.
- (20) J. J. Rush and H. E. Flotow (1968), *J. Chem. Phys.* 48, 37.
- (21) S. T. Picraux and F. L. Vook (1974), *Phys. Rev. Lett.* 33, 1216.
- (22) E. A. Weaver (1967), *J. Chem. Phys.* 47, 4891.
- (23) H. M. Laska, R. H. Doremus, and P. J. Jorgensen (1969), *J. Chem. Phys.* 50, 135.
- (24) H. Matzke (1967a), *Z. Naturforsch.* A22, 965.
- (25) P. J. Jorgensen and F. J. Norton (1969), *Phys. Chem. Glasses* 10, 23.
- (26) J. Crank and G. S. Park, ed. (1968), *Diffusion in Polymers*, Academic Press, New York.
- (27) D. G. Thomas and J. J. Lander (1956), *J. Chem. Phys.* 25, 1136.
- (28) G. R. Caskey, Jr. (1974b), *Mater. Sci. Eng.* 14, 109.
- (29) T. Smith (1962), Report NAA-SR-6267.
- (30) T. S. Elleman, Unpublished data.
- (31) H. Gauss (1965), *Z. Naturforsch.* A20, 1298.
- (32) D. G. Hurst (1962), Report CRRP-1124, Atomic Energy of Canada, Ltd.
- (33) A. McNabb and P. K. Foster (1963), *Trans. Met. Soc. AIME* 227, 618.

- (34) R. A. Oriani (1970), *Acta Met.* 18, 147.
- (35) A. Sy Ong and T. S. Elleman (1970), *Nucl. Instrum. Methods* 86, 117.
- (36) M. Koiwa (1974), *Acta Met.* 22, 1259.
- (37) A. Lawley, W. Liebmann, and R. Maddin (1961), *Acta Met.* 9, 841.
- (38) A. L. Eustace and O. N. Carlson (1961), *Trans. Met. Soc. AIME* 221, 238.
- (39) B. A. Wilcox and R. A. Huggins (1960), *J. Less Common Metals* 2, 292.
- (40) M. R. Louthan, Jr., G. R. Caskey, Jr., J. A. Donovan, and D. E. Rawl (1972), *Mater. Sci. Eng.* 10, 357.
- (41) C. Baker and H. K. Birnbaum (1972), *Scripta Met.* 6, 851.
- (42) J. S. Blakemore (1970), *Met. Trans.* 1, 145.
- (43) L. M. Clarebrough, P. Humble, and M. H. Loretto (1967), *Acta Met.* 15, 1004.
- (44) C. Baker and H. K. Birnbaum (1973), *Acta Met.* 21, 865.
- (45) S. Harper, J. A. Callcut, D. W. Townsend, and P. Eborall (1961), *J. Inst. Metals* 90, 414.
- (46) H. G. Ellerbrock, G. Vibrans, and H. P. Stüwe (1972), *Acta Met.* 20, 53.
- (47) H. Matzke (1967b), *Z. Metallk.* 58, 572.
- (48) H. Migge (1967), *Phys. Status Solidi* 35, 673.
- (49) G. R. Caskey, Jr. and W. L. Pillinger (1975), *Met. Trans.* A61, 467.
- (50) P. K. Foster, A. McNabb, and C. M. Payne (1965), *Trans. Met. Soc. AIME* 233, 1022.

- (51) S. W. Stafford and R. B. McLellan (1974), *Acta Met.* 22, 1463.
- (52) M. R. Louthan, Jr., J. A. Donovan, and G. R. Caskey, Jr.
(1975), *Acta Met.* 23, 745.
- (53) G. R. Caskey, Jr. and R. G. Derrick (1974), presented at the
Spring Meeting of the Metallurgical Society, Pittsburgh, PA,
May 1974.
- (54) K. Shiraishi and R. Nagasaki (1965), *J. Nucl. Sci. Technol.* 2,
499.
- (55) O. D. Gonzales (1969), *Trans. Met. Soc. AIME* 245, 607.
- (56) G. R. Caskey, Jr., M. R. Louthan, Jr., and R. G. Derrick
(1975), *J. Nucl. Mater.* 55, 279.
- (57) G. C. Smith (1974), in *Hydrogen in Metals*, I. M. Bernstein
and A. W. Thompson (ed.), American Society of Metals, Metals
Park, Ohio.
- (58) C. Sykes, H. H. Burton, and C. C. Gregg (1947), *J. Iron Steel*
Inst. 156, 155.
- (59) R. E. Howard and A. B. Lidiard (1964), *Rep. Prog. Phys.* XXVII,
161.
- (60) J. S. Kirkaldy (1970), *Adv. Mater. Res.* 4, 55.
- (61) M. Weinstein and J. F. Elliott (1963), *Trans. Met. Soc. AIME*
227, 382.
- (62) F. E. Wooley and R. D. Pehlke (1965), *Trans. Met. Soc. AIME*
233, 1454.
- (63) D. W. Rudd, D. W. Vose, and S. Johnson (1961), *J. Phys. Chem.*
65, 1018.

- (64) H. C. Savage and R. A. Strehlow (1973), *Trans. Amer. Nucl. Soc.* 17, 152.
- (65) J. H. Austin, T. S. Elleman, and K. Verghese (1973), *J. Nucl. Mater.* 48, 307.
- (66) M. R. Louthan, Jr. and R. G. Derrick, to be published in *Corrosion Sci.*
- (67) C. W. Pennington, K. Verghese, and T. S. Elleman (1973), *Trans. Amer. Nucl. Soc.* 17, 151.
- (68) S. Dushman (1962), *Scientific Foundation of Vacuum Technique*, 2nd Ed., Wiley, New York.
- (69) W. A. Swansiger, R. G. Musket, L. J. Weirick, and W. Bauer (1974), *J. Nucl. Mater.* 53, 307.
- (70) R. A. Strehlow and H. C. Savage (1974), *J. Nucl. Mater.* 53, 323.
- (71) J. H. Austin and T. S. Elleman (1972), *J. Nucl. Mater.* 43, 119.
- (72) G. R. Caskey, Jr. (1974a), in *Hydrogen in Metals*, I. M. Bernstein and A. W. Thompson (ed.), American Society of Metals, Metals Park, Ohio.
- (73) M. R. Piggot and A. C. Siarkowski (1972), *J. Iron Steel Inst.* 210, 901.
- (74) R. Ash, R. M. Barrer, and D. G. Palmer (1965), *Brit. J. Appl. Phys.* 16, 873.
- (75) D. L. Johnson, N. M. Bashra, and L. C. Tao (1971), *Mater. Sci. Eng.* 8, 175.
- (76) P. Kofstad (1966), *High Temperature Oxidation of Metals*, John Wiley, New York.

- (77) M. T. Hepworth and R. Schumann (1962), *Trans. Met. Soc. AIME* 224, 928.
- (78) R. Hales (1971), *J. Phys. Chem. Solids* 32, 1417.
- (79) R. Hales, P. S. Dobson, and R. E. Smallman (1969), *Acta Met.* 17, 1323.
- (80) D. K. Reimann and J. P. Stark (1970), *Acta Met.* 18, 63.
- (81) T. Ichimiya and A. Furichi (1968), *Int. J. Appl. Radiat. Isotopes* 19, 575.
- (82) L. C. Beavis (1973), *J. Vac. Sci. Technol.* 10, 386.
- (83) H. K. Birnbaum (1973), *Scripta Met.* 7, 925.
- (84) D. R. Begeal (1975), *J. Vac. Sci. Technol.* 12, 405.
- (85) V. Srikrishnan, H. W. Liu, and P. J. Ficalora (1975), *Scripta Met.* 9, 663.
- (86) G. Sicking and H. Buchold (1971), *Z. Naturforsch.* A26, 1973.
- (87) K. F. Chaney and G. W. Powell (1970), *Met. Trans.* 1, 2356.
- (88) L. Katz, M. Guinan, and R. J. Borg (1971), *Phys. Rev. B* 4, 330.
- (89) M. R. Louthan, Jr., J. A. Donovan, and G. R. Caskey, Jr. (1974), *Scripta Met.* 8, 643.
- (90) C. R. Copp and P. Flubacher (1962), *J. Nucl. Mater.* 6, 213.
- (91) M. R. Louthan, Jr., and G. R. Caskey, Jr., paper in preparation.
- (92) W. Geller and Tak-Ho-Sun (1950), *Arch. Eisenhuettenw.* 21, 423.
- (93) T. M. Stross and F. C. Tompkins (1956), *J. Chem. Soc.*, 230.
- (94) W. Eichenauer, H. Künsig, and A. Pebler (1958), *Z. Metallk.* 49, 220.
- (95) M. L. Hill and E. E. Johnson (1959), *Trans. Met. Soc. AIME* 215, 717.

- (96) R. C. Frank, D. E. Swets, and D. L. Fry (1958), *J. Appl. Phys.* 29, 892.
- (97) R. M. Barrer (1940), *Trans. Faraday Soc.* 36, 1242.
- (98) P. L. Chang and W. D. G. Bennett (1952), *J. Iron Steel Inst.* 170, 205.
- (99) H. Schenck and H. Taxhet (1959), *Arch. Eisenhuettenw.* 30, 661.
- (100) J. K. Gorman and W. R. Nardella (1962), *Vacuum* 12, 19.
- (101) W. L. Bryan and B. F. Dodge (1963), *J.A.I.C.H.E.* 9, 223.
- (102) R. Wagner and R. Sizman (1964), *Z. Angew. Physik* 18, 193.
- (103) O. D. Gonzales (1967), *Trans. Met. Soc. AIME* 239, 929.
- (104) D. Randall and O. N. Salmon (1953), USAEC Report KAPL-904.

FIGURE 1. Diagrammatic Representation of Interrelations Among Tritium Diffusion, Surface Effects, and Radiation

FIGURE 2. Diffusivity of Tritium in Various Materials

FIGURE 3. Effect of Metallurgical Conditions on the Apparent Solubility of Tritium in Nickel

FIGURE 4. Apparent Diffusivity of Hydrogen in α -Iron

FIGURE 5. Permeability of Hydrogen in α -Iron

a. Iron Oxides

b. Chromium, Niobium, and Molybdenum Oxides

FIGURE 6. Temperature Dependence of the Equilibrium Pressure Ratio (p_{H_2O}/p_{H_2})

FIGURE 7. Tritium Concentration as a Function of Depth into Rods

TABLE 1. Effects of Trapping and Surface Films on Permeation

	<u>Reversible Trapping</u>	<u>Irreversible Trapping</u>	<u>Continuous Film</u>
Steady-State Permeation Rate (P_{∞})	$P_{\infty} = P_{\infty} \text{ (ideal)}$	$P_{\infty} = P_{\infty} \text{ (ideal)}$	$P_{\infty} < P_{\infty} \text{ (ideal)}$
Apparent Diffusivity (D^*)	$D^* < D_L$	$D^* < D_L^{\alpha}$	$D^* < D_L$
Instantaneous Permeation Rate (P_t)	$P_t < P_t \text{ (ideal)}$	$P_t < P_t \text{ (ideal)}$	$P_t < P_t \text{ (ideal)}$
Instantaneous Evolution Rate (E_t)	$E_t > E_t \text{ (ideal)}$	$E_t = E_t \text{ (ideal)}$	$E_t < E_t \text{ (ideal)}$

α . D_L = true lattice diffusivity.