

FORMATION AND USE OF OXIDE FILMS TO IMPEDE OUTGASSING OF METALS*

R. A. Strehlow and H. C. Savage
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

Abstract

Phenomena associated with the outgassing of metals are generally interpreted using models based either on desorption of compounds from the surface or on diffusion of dissolved gases from the interior of the metal. It is generally recognized that surface oxide films can serve to decrease outgassing rates of metals. However, the processes associated with the outgassing of oxidized or oxide-coated metals are not well understood. Outgassing of oxidized metals is considered in light of the results of recent studies of hydrogen permeation through metals with well characterized oxide films. The chemical stabilities of the oxides as well as the physical imperfections of the film are considered. A model is suggested for the expected outgassing behavior of oxidized steels at intermediate temperatures, which are of interest in the design of controlled thermonuclear research experiments and reactors. The role of impurities and the usefulness of specialized oxidation treatments are discussed.

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The choice of materials for use in ultra high vacuum systems is governed largely by the requirement that the rate of outgassing of hydrogen be reduced to a low enough value that the desired background or base pressure conditions can be obtained.¹ This requirement is especially severe for controlled thermonuclear devices and reactors in which the purity of tritium must be controlled and in which the vacuum enclosures may need to be operated at elevated temperatures. Many methods have been used to reduce the gas load in vacuum systems arising from the outgassing of metals.² Among these methods are included numerous cleaning techniques, coating methods, and in situ baking procedures. One type of coating, which has been recognized as being efficacious in reducing the outgassing of a metal is an oxide film.³ Although various methods have been reported in the literature for forming oxides^{1,4}, the extent of reduction of outgassing by such films has not been extensively studied. In fact, although the reduction of outgassing appears to be well established, reported results are quite variable. It seems likely that one of the reasons for this variability is the fact that the oxides usually formed on a metal are formed by a method involving a high oxidation potential, e.g. electro-anodization or air oxidation.^{1,4} Under the conditions of the usual vacuum

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environment where the oxidation potential is much lower, many oxides would not be expected to be stable. Recent work, however, at this Laboratory on the permeation of deuterium through metals with oxide films suggests that very low and constant outgassing rates might be obtained if the metal is oxidized at a low and controlled potential to obtain a highly impermeable and stable oxide.⁵ For example, we have observed as much as a thousandfold decrease in permeation rate of deuterium at one torr driving pressure through metals which were oxidized at elevated temperatures (600°C) using deuterium which had been saturated with D₂O vapor at 25°C. The present discussion is an attempt to describe the outgassing behavior of a metal oxidized in this, or a similar, manner.

Since the principal gas flow from an oxidized metal is expected to occur through the pores and cracks in the oxide,⁵ a different theoretical description of outgassing is required from that which is usually employed. General treatments of outgassing phenomena take the solution of the diffusion equation in one dimension as a theoretical foundation.^{6,7} The diffusion equation as usually employed is not appropriate, however, when the outgassing is impeded by an oxide film. The reason for this is that the diffusion equation is normally written for a simple slab geometry. Based on this boundary condition, a uniform concentration gradient is expected to be developed in the metal as outgassing proceeds. If, however, the metal is covered by an impermeable oxide film containing defects like pores or cracks, the concentration gradient in the metal will never be uniform through the thickness of the metal but will be expected to exist in three dimensional geometry and be small except near the interface of the metal and oxide film. As far as outgassing is concerned, the hydrogen initially dissolved in the metal will then act as though it were a trapped volume of gas being released to the vacuum system through a restriction.

Before considering several cases of outgassing, it is necessary to develop a relation between the steady-state hydrogen permeation rate and the detailed geometry of the cracks or pores assuming the oxide film itself to be impermeable. It is not necessary to proceed with a full treatment of the diffusion equation in three dimensions, since the relationships have been derived for the strictly analogous case of constriction electrical resistance. These relationships for electrical constriction resistance relate resistance to simple geometrical parameters of defects in an insulating film. The average pore diameter and the average spacing of pores in an otherwise highly resistive film are examples of the geometrical parameters which have been considered.⁸ The procedure followed here is to identify and define the resistance to permeation of unoxidized metal and, then, the resistance due to constrictions. Adding these resistances together yields a relation between the permeation flux and the parameters used to characterize the constrictions. It will be seen that the permeation relations derived in this fashion can be simplified and easily related to outgassing rates.

First, we consider the one dimensional permeation of hydrogen through a slab of unoxidized metal of uniform thickness x . Throughout this discussion we will assume a constant temperature and will neglect end effects. If this slab of metal separates two volumes in which the hydrogen partial pressures are P_1 and P_2 with P_2 greater than P_1 , and if the hydrogen concentration in the metal at each surface is that defined by the Sieverts' equilibrium solubility, the steady-state permeation flux of hydrogen through the metal, J_m , can be written as:⁵

$$-J_m = \frac{DK_s}{x} (P_2^{1/2} - P_1^{1/2}) \quad (1)$$

where D is the diffusivity of hydrogen in the metal with dimensions $[L^2/t]$, in which L is distance and t is time. The Sieverts' constant K_s relates the square root of hydrogen pressure to concentration of hydrogen in the metal:

$$C = K_s P^{1/2} \quad (2)$$

Noting that the flux, J_m , is equivalent to a current density, we may write from Eq. (1)

$$-J_m A = -I = \frac{DAK_s}{x} (P_2^{1/2} - P_1^{1/2}) \quad (3)$$

in which I is the current of permeating hydrogen having dimensions of a quantity per unit time and A is the area. The term $(P_2^{1/2} - P_1^{1/2})$ in Eq. (3) may be viewed as the driving potential for permeation. Hence, by analogy with Ohm's Law, the resistance to permeation flow, R_m , is:

$$R_m = x/DAK_s \quad (4)$$

The constriction resistance may be taken from Holm (Ref. 8, Eq. 5.08, p. 23) for a set of circular holes or pores through which flow occurs. The pores are of average radius, a , and average separation, 2ℓ . Following Holm,⁸ we obtain

$$R_c = \frac{2\ell^2}{DAK_s a \pi} \tan^{-1} \frac{\ell}{a} - \frac{\ell}{DAK_s} \quad (5)$$

If we assume that the radii of the pores are small relative to the distance between pores, $a \ll \ell$ and $\tan^{-1} \frac{\ell}{a} = \frac{\pi}{2}$; thus, Eq. (5) can be simplified to yield

$$R_c = \frac{\ell^2}{DAK_s a} - \frac{\ell}{DAK_s} \quad (6)$$

in which the constriction resistance, R_c , is seen to have the same dimensions as the metal resistance, R_m , in Eq. (4). (The area, A , is introduced in Eqs.

(3) through (6) to assist in maintaining clarity in the derivation and to distinguish it from the symbol, a , representing the average pore radius.) The total resistance to permeation through the oxide-film metal is obtained by adding Eqs. (4) and (6); thus,

$$R_{\text{total}} = R_m + R_c = \frac{x + (\frac{\ell^2}{a}) - \ell}{DK_s} . \quad (7)$$

Based on the foregoing, it is easily seen that the steady-state permeation flux of hydrogen through the oxide-film metal is

$$-J = \frac{DK_s}{(x + \frac{\ell^2}{a} - \ell)} (P_2^{1/2} - P_1^{1/2}) . \quad (8)$$

With $\ell \gg a$ (as we have assumed), and, if the permeation impedance is offered principally by the oxide film, we may neglect both x and ℓ in comparison with ℓ^2/a and obtain:

$$-J = \frac{aDK_s}{\ell^2} (P_2^{1/2} - P_1^{1/2}) . \quad (9)$$

We have subjected Eq. (9) to only one test so far. Oxidation of a sample of type 406 stainless steel with the D_2O - D_2 mixture resulted in a permeation flow rate that was 600 times lower than that of 1-mm-thick unoxidized metal.⁵ Examination of a series of scanning electron micrographs of the oxidized surface showed that a set of somewhat elongated pores existed with an estimated spacing (2ℓ) of 0.04 cm and an estimated average radius of 3×10^{-5} cm. These pores appeared to be associated with machining defects of the specimen. From the measured values of the spacing and radii we calculate a value of ℓ^2/a equal to $(0.02)^2/(3 \times 10^{-5})$ cm = 13 cm. The permeation data would have led us to expect a value of 60 cm. However, the agreement is quite reasonable in view of the crudity of the measurements.

We may express the relation shown as Eq. (9) in terms of concentrations rather than pressures by substitution of Eq. (2) and obtain

$$-J = \frac{aD}{l^2} (C_2 - C_1) \quad (10)$$

in which the flux is given as a function of the diffusivity (D), the average radius a of pores separated by the distance $(2l)$, the hydrogen concentration in the bulk of the metal (C_2), and the concentration of hydrogen dissolved in the metal in immediate contact with the hydrogen gas in the downstream volume, i.e. the vacuum system, (C_1).

An equation similar to Eq. (5) can be derived from equations 4.23 and 4.27 of Reference 8 for constriction resistance for long parallel cracks. This equation is

$$R_c' = \frac{k \ln (2\alpha/\beta)}{DAK_s} \quad (11)$$

in which k is the average crack separation and α/β is the average crack width to length ratio. In this presentation, however, we will use the pore geometry and Eq. (10) to illustrate the application to outgassing.

Several types of outgassing behavior may be distinguished depending on such factors as whether one or two surfaces of the metal are oxidized, whether the metal has more than an equilibrium concentration of hydrogen dissolved in it, and whether the metal is corroding according to any of several possible mechanisms involving water as the oxidant. We will consider briefly four outgassing situations:

- (1) A volume of metal, filmed by oxide, is immersed in the vacuum system environment;

- (2) A metal forms part of the boundary of the vacuum system, is in equilibrium with the hydrogen in the atmosphere, and is oxidized on either or both surfaces;
- (3) The metal forms part of the boundary of the vacuum system and contains hydrogen in greater than equilibrium amounts;
- (4) A metal forming a boundary corrodes with generation of hydrogen and contains impeding oxide layers at both surfaces of the metal.

Beginning with the first case above, we may view the outgassing as equivalent to the pumping out of a trapped volume and can write

$$q = \frac{GDc_0}{xl^2} \tag{12}$$

in which q is the instantaneous outgassing rate of one cm^2 of a slab of thickness x , C is the concentration of hydrogen in the metal, and G is a geometrical factor equal to 2 for the stipulated geometry. It should be noted that the outgassing rate q is to be identified with the absolute value of the flux. The symbol q is used to conform to conventional usage. The concentration changes in accordance with the relation

$$\frac{dC}{dt} = - \frac{D(C - C_s)a}{xl^2} \tag{13}$$

in which C_s is the steady-state concentration, x is the thickness of the slab and accounts, as in Eq. (12), for the initial quantity of hydrogen in the specimen, t is the time, and the other terms have been previously defined. Integrating Eq. (13), letting $C_s = 0$, and substituting the result into Eq. (12) yields the following expression for q as a function of time

$$q = \frac{2DaC_0}{xl^2} [\exp(-Dat/xl^2)] \tag{14}$$

in which C_0 is the initial hydrogen concentration in the metal. Similar expressions can be derived readily for other geometries.

The second case listed above is a general case for vacuum systems, where a sheet of metal forms part of the boundary of the vacuum system, is in equilibrium with hydrogen in the atmosphere, and is oxidized on either one or both of its surfaces. If the metal is oxidized on the surface contiguous with the vacuum region only, the establishment of steady-state permeation should be rapid and the steady-state flux should be given by Eq. (9) above. The usual partial pressure of hydrogen in the atmosphere is about 4×10^{-4} torr.³ If we assume that the vacuum system produces a negligibly low partial pressure of hydrogen, and that DK_s is equal to 3×10^{-9} torr-liters(NTP)/cm-sec-torr^{1/2} (which is the case for many structural steels at $400^\circ\text{C}^{3,5}$), we obtain from Eq. (9) an expected outgassing rate of 6×10^{-13} torr-liters(NTP)/sec-cm². Since the usual pumping speeds of vacuum systems for hydrogen rarely exceed 0.1 liters/sec-cm² (and may be much less for thermonuclear devices and reactors), the potential value of an impeding oxide film is seen to be especially great at elevated temperatures if equivalent protium partial pressures less than 10^{-9} torr are desired. At normal ambient temperatures, the protium partial pressure may not be inconveniently high, even in the absence of a film.

If a metal sheet forms part of the vacuum system boundary and is oxidized on both surfaces, the expected transient outgassing rate derived from Eqs. (10) and (13) is

$$C = C_s + (C_0 - C_s) \exp(-Dat/\lambda l^2) \quad , \quad (15)$$

in which C_s is the steady-state hydrogen concentration in the metal which can be computed using Eq. (9) if appropriate values for $a/\lambda l^2$ are known for the two surfaces.

The third case listed above was for the situation where the metal forms part of the boundary of the vacuum system and contains hydrogen in greater than equilibrium amounts. This case is common for vacuum systems which are operated without baking. For thermonuclear application, however, this type of outgassing behavior is expected chiefly in tritium handling systems where tritium at significant partial pressures will be cycled extensively. We have observed significant memory effects in tritium handling systems which we attribute to this type of behavior. The time constants for these memory effects will be related both to the interchange of tritium with adsorbed water and can be obtained from equations similar to Eq. (15). The observations we have made so far permit only the conclusion that the usual diffusion equations do not allow us to calculate the tritium behavior in these systems.

The fourth case of outgassing listed above needs to be mentioned although the situation is quite complex. This is the case for a metal which forms a boundary of a vacuum system and which is corroding at some rate with the generation of hydrogen. When the metal is oxidized, the hydrogen will be generated at the metal-oxide interface nearest the ambient environment. Depending upon the detailed consideration of the diffusion paths and the a/l^2 parameters for the two films, a large fraction of the hydrogen formed by the corrosion process can permeate and dominate the outgassing. There has been little experimental work in this area.

Experimentally, we have found⁵ that the chemical stabilities of films are important to the maintenance of an oxide film that impedes hydrogen permeation at elevated temperatures. This factor is likely to be important for any application of oxide films to impede outgassing at the elevated temperatures of interest in the design of thermonuclear reactors. The considerations presented here show that outgassing behavior can probably

be analyzed in terms of the simple model implying the presence of an impermeable film with pores or cracks. So far this model has only been subjected to a few tests as applied to permeation of hydrogen through metals, and none with respect to outgassing. Recognizing that permeation rates can be significantly reduced by oxides films, however, leads to the conclusion that outgassing also may be controlled in a similar manner. The problems which must be faced include, of course, the verification of the model described here as well as a more extensive consideration of the chemical stabilities of oxide films which might be formed on metals of interest in thermonuclear devices and reactors.

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