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ENHANCED SELECTIVE HYDROGEN DESORPTION FROM METALS

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CONTRACT # DE-AC02-76-CHO-3073

ABSTRACT

The thermal desorption of hydrogen isotopes from a metal is usually a second order process, the rate for which becomes asymptotically slow. We present a method for enhancing the desorption rate of one particular isotope by maintaining a constant pressure of another molecular species. This results in an effective first order desorption and concomitant exponential decay of the concentration of the selected isotope. Data is presented for the enhanced desorption of deuterium from a Zr-Al getter. The results agree well with a theoretical model, which is discussed. This enhanced desorption method should be particularly useful for tritium operation in the Tokamak Fusion Test Reactor.

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I. INTRODUCTION

The thermal desorption of hydrogen from a metal, such as a getter, is frequently rate limited by the surface reaction kinetics.¹ For dilute hydrogenic concentrations, the surface kinetics are second order in the concentration. This results in an asymptotically slow decrease of the hydrogen loading.² We have investigated a technique for enhancing the desorption rate of a specific isotope by maintaining a constant concentration of another isotope. This results in an effective first order desorption for the particular isotope, which in turn, causes the concentration of that isotope to decrease exponentially.

In Sec. II we present the formalism necessary for understanding the details of these processes and for interpreting the data which are reported in Sec. III. Sec. IV provides a summary and discussion.

Such enhanced selective desorption will be particularly useful for operation of Zr-Al getters in the Tokamak Fusion Test Reactor (TFTR).³ The tritium absorbed by the Zr-Al getters in TFTR can be desorbed in a much shorter time and to much lower residual concentrations. Other applications include selectively desorbing deuterium in a system requiring helium leak detection.

II. THEORY

A detailed discussion of the theory of bulk getter operation is given in Ref. 4. We present here the salient features of the desorption formalism. The diffusion of hydrogen in the getter can be the rate-limiting process for times $\sim L^2/D$, where L is the getter thickness and D is the bulk diffusivity. For the Zr-Al getter which we consider here, however, this time is short^{1,5} compared to the total desorption time, and we will therefore not consider the

effects of diffusion in this work. To facilitate comparison with our experimental results, we will discuss the particular case of deuterium desorption. The derivations which follow are, of course, entirely general.

The equation describing the surface kinetics of D_2 interacting with a planar getter of material G is

where k_i and k_o are, respectively, the absorption and desorption rates per unit surface area. The incident absorbed flux Γ_i is then

$$\Gamma_i = k_i P \quad , \quad (2)$$

where P is the D_2 pressure. The desorption flux Γ_o is

$$\Gamma_o = k_o q_D^2 \quad , \quad (3)$$

where q_D is the deuterium concentration at the surface which we will express in Torr-l/g. The assumption that diffusion is not rate-limiting implies that the concentration is uniform throughout the bulk and is therefore equal to q_D . The net flux out of the getter is Γ where

$$\Gamma = \Gamma_o - \Gamma_i \quad . \quad (4)$$

A back up pump of deuterium speed S is utilized to pump the net desorbed flow. Ignoring transients which decay in the typically short time $\sim V/S$ where V is the chamber volume, we can write the usual vacuum equation⁶

$$A\Gamma = PS, \quad (5)$$

where A is the area of the getter. From these equations we can find the relationship between P and q_D during desorption:

$$P = (S_T/S) K q_D^2, \quad (6)$$

where $K \equiv k_o/k_i$ is the equilibrium constant. S_T is the effective series pumping speed given by

$$\frac{1}{S_T} = \frac{1}{S} + \frac{1}{S_G}, \quad (7)$$

with $S_G \equiv A k_i$ the initial getter deuterium pumping speed. The above equations hold for non-planar getters with S_G taken to be the actual pumping speed. From the conservation of particles $M(dq/dt) = -A\Gamma$, and therefore from Eqs. (5) and (6) we have

$$\frac{dq_D}{dt} = -\alpha q_D^2, \quad (8)$$

where

$$\alpha = \frac{S_T K}{M}, \quad (9)$$

and M is the getter mass. The solution of Eq. (8) for $q_D(t)$, the concentration at time t, is

$$q_D(t) = (\alpha t + q_D(0)^{-1})^{-1} . \quad (10)$$

This solution for second order desorption predicts that the concentration decreases as t^{-1} with the rate slowing as t^{-2} .

We now explore the desorption of deuterium in the presence of a constant pressure of H_2 . Eq. (1) is now replaced by the four reactions:

where Eq. (14) includes both gas phase and surface reactions. The solution to the coupled Eqs. (11)-(14) is very complicated. To see the important features of the enhanced selective desorption, we will make the simplifying assumption that $q_H \gg q_D$. Then if the H_2 pressure is held constant, the desorption of deuterium will be dominated by the reaction Eq. (12), and we can ignore the reactions in Eqs. (13) and (14). The reaction in Eq. (11) will be nominally in equilibrium. The HD flux into the getter is Γ'_1 where

$$\Gamma'_1 = k'_i P' , \quad (15)$$

with P' the HD pressure. The flux out will be Γ'_o :

$$\Gamma'_C = k'_O q_H q_D . \quad (16)$$

The pressure P' during desorption is

$$P' = (S'_T/S') K' q_H q_D , \quad (17)$$

where S'_T and S' are the respective pumping speeds for HD in analogy with Eq. (7) and $K' = k'_O/k'_1$. The resultant equation for q_D during this enhanced desorption is

$$\frac{dq_D}{dt} = -\beta q_D , \quad (18)$$

where the constant β is

$$\beta = \frac{S'_T K'}{2M} q_H . \quad (19)$$

The solution to Eq. (18) is

$$q_D(t) = q_D(0) \exp(-\beta t) . \quad (20)$$

Thus $q_D(t)$ falls exponentially, since the deuterium desorption is effectively first order.

III. EXPERIMENTAL RESULTS

The experiments were performed using a standard SAES Zr-Al alloy (St1010) nonevaporable bulk getter module⁷ with a measured Zr-Al mass of 120 ± 5 g. The module was contained in a stainless steel vessel of 166 l pumped by a

turbomolecular pump with a measured H_2 speed of 340 l/s in the molecular flow regime. Hydrogen and deuterium were introduced into the chamber through separate piezo-electric valves and a common calibrated conductance. A differential capacitance manometer was used to measure the pressure drop across this conductance. From this measurement, both the flow rate and the total gas quantity were determined. The H_2 pressure was held constant by feedback control of the H_2 piezo-electric valve. A quadrupole mass analyzer was used to monitor the behavior of the mass 2 and mass 3 signals. The analyzer was located in a separately pumped chamber connected to the main chamber by a small conductance leak valve facilitating measurements at high H_2 pressures in the main chamber. Prior to an experimental run, the ratio of the mass 3 to mass 2 signal was $\sim 2 \times 10^{-4}$.

The getter was activated by heating to 700°C for 45 min. Following activation, and with the getter at 20°C, the base pressure in the main chamber was 6×10^{-10} Torr. Experiments were performed for getter temperatures in the range of 600°C-740°C, with the hydrogen concentration in the range from 0.2 to 2.5 Torr-l/g.

During desorption, q_D was inferred from the HD partial pressure using Eq. (17). Fig. 1 shows the temporal behavior of q_D with the getter at 670°C, $q_D(0) = 0.23$ Torr-l/g, and a hydrogen pressure of 7×10^{-4} Torr. The resulting hydrogen concentration is $q_H = 0.96$ Torr-l/g. From previous results,⁸ we calculate that the HD equilibrium constant K' is

$$K' = 1.79 K_H, \quad (21)$$

where K_H is the measured H_2 equilibrium constant.⁸ Using this value for K' we have plotted the predicted q_D behavior [Eq. (20)] in Fig. 1 also. The data

exhibit an exponential decay which is in excellent agreement with the predicted behavior over four e-foldings. At lower values of q_D , the observed decay rate decreases. This change in slope has been observed over the entire range of parameters and occurs when the ratio of mass 3 to mass 2 signals is $\sim 3 \times 10^{-3}$ independent of getter temperature. When this slower decay rate occurred, the same ratio of mass 3 to mass 2 was observed when the leak valve to the quadrupole was closed. This shows that deuterium is desorbed from the mass spectrometer chamber walls. It is likely that a similar phenomenon occurs in the main chamber. Therefore, we presume that these are the sources of the residual mass 3 signal. Also shown in Fig. 1 is the usual second order desorption along with the prediction from Eq. (10). In this case the getter was loaded to $q_D(0) = 0.24$ Torr-l/g and desorbed without H_2 gas. After 5×10^3 s, the deuterium concentration has decreased by only 1.1 e-foldings showing the asymptotically slow desorption.

In Fig. 2 are plotted the measured values of the decay rate γ vs. the values predicted from Eq. (19). The values used for S were determined from the measured flow and pressure. Good agreement is obtained, although some deviation is observed at the largest H_2 pressure (2×10^{-2} Torr), where viscous effects may modify the results.

IV. SUMMARY AND DISCUSSION

We have shown theoretically and experimentally that the desorption of a selected hydrogen isotope can be effectively first order by providing a constant partial pressure of a second isotope. The resulting exponential decay rate is in close agreement with that predicted theoretically. Deviations of this rate are observed at small values of the HD to H_2 partial pressure ratio independent of the getter temperature; however, this is likely due to desorption from the vessel walls.

While a detailed discussion of the implications of this enhanced process is not possible here, we note a few illustrative comparisons for a bulk getter. We assume that the initial concentration of the selected isotope is 0.20 of that for the constant pressure species. Then, if it is desired to desorb 90% of the selected isotope, the enhanced desorption can be effected in one tenth the time required for conventional desorption at the same getter temperature. Desorption to the 99% level is more than 50 times faster. Equivalently, in the same time required for conventional desorption to achieve 50%, the enhanced process would result in 92% desorption. These examples show that the selective desorption of tritium from the TFTR Zr-Al getters can be achieved more quickly and to a lower practical level using the enhanced process. Finally, to the extent that tritium desorption from the vacuum vessel walls of a fusion device is limited by surface kinetics, the method discussed in this work should be effective in achieving lower tritium wall inventories in shorter times.

ACKNOWLEDGMENTS

We wish to thank J. Stanton for assistance in data collection and analysis, and E. Pinelli for technical support. This work was supported by U.S. Department of Energy Contract DE-AC02-76-CHO3073.

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FIGURE CAPTIONS

- Fig. 1. Measured and predicted time dependence of the getter deuterium concentration for the getter desorbing at 670°C and initially loaded to $q_D(0) = .23$ Torr l/g. Both enhanced desorption in the presence of hydrogen at $P = 7 \times 10^{-4}$ Torr and normal desorption are shown.
- Fig. 2. Measured exponential decay rates (solid circles) for enhanced desorption compared to the predicted rate (solid line) for different values of β over the temperature range of 600°C to 740°C, and hydrogen concentration range of 0.2 to 2.0 Torr-l/g.

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Fig. 1

Fig. 2