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PRESSURE DEPENDENCE OF Zr-Al PUMPING SPEED FOR H_2

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ABSTRACT

We have measured the pumping speed of the Zr-Al alloy bulk getter over a pressure range of 10^{-5} to 10^{-2} Torr. The temporal evolution of the pumping speed follows closely the behavior predicted by a theoretical model for bulk gettering. In particular, for pressure P above $\sim 5 \times 10^{-3}$ Torr, the pumping speed decreases as $P^{-1/2}$. From the high pressure data, we have measured the bulk diffusivity of H in Zr-Al to be $D = \exp [-4.0(1.1) - 9100(450)/T] \text{ cm}^2 \text{ s}^{-1}$ with T the getter temperature in $^{\circ}\text{K}$. This is in good agreement with values obtained from desorption measurements.

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I. INTRODUCTION

Zr-Al alloy (St101®)¹ nonevaporable bulk getters are used in tokamak fusion devices for pump limiters,² turbomolecular pump back-up,³ and in-torus control of hydrogenic recycling and impurities.⁴ In these applications the hydrogenic pressure can be high enough so that bulk diffusion will affect the pump operation, as opposed to the usual regime, where the surface reaction kinetics are rate-limiting.⁵ The salient consequence of the diffusion-limited operation is that the pumping speed is pressure dependent. In this paper we explore the behavior of the Zr-Al H₂ pumping speed S over the pressure range of 10⁻⁵-10⁻² Torr. Data for the temporal evolution of S at constant pressure are in good agreement with that predicted by a bulk getter model,⁵ which includes both surface reactions and bulk diffusion. From the high pressure data we have determined the H diffusivity in Zr-Al and find that it agrees well with that derived from desorption measurements.⁶

In Sec. II we summarize the theory used to interpret our measurements. The experimental apparatus and procedures are discussed in Sec. III. Results are presented and compared to the theoretical predictions in Sec. IV. A summary follows in Sec. V.

II. THEORY

In this paper we analyze our data using a theory of bulk getter operation described in detail elsewhere.⁵ We summarize here the relevant features of the theory.

The surface reaction of H₂ and Zr-Al is described by the reaction

where k_1 and k_0 are, respectively, the absorption and desorption rates per unit area, with the equilibrium constant $K = k_0/k_1$. The behavior of hydrogen in the bulk is described by a diffusion equation with diffusivity D utilizing the implied fluxes at the surface [Eq.(1)] as boundary conditions. The pumping speed S follows from the usual equation for particle conservation at constant pressure:

$$S = \frac{F}{P}, \quad (2)$$

where F is the net flow into the getter, which is determined by the solution to the diffusion equation with the boundary flux conditions.

The characteristic behavior of S is governed by the dimensionless parameter H given by

$$H = \frac{S_0 P/A}{D q_0 \rho / L}, \quad (3)$$

where S_0 is the initial getter pumping speed, A is the area, q_0 is the equilibrium concentration (expressed in units of inverse mass); ρ is the Zr-Al density, and L is the getter thickness. For the present calculations, we take values for D and K from Refs. 6 and 7 respectively. We have measured L to be 120 μm and ρ to be 3.0 g/cm^3 . The initial pumping speed S_0 was measured from the initial flow and from the transient decay of an H_2 pulse. It was noted to have a slight temperature dependence with an activation energy of ~ 0.1 kcal/mole. Since this is a small effect, we ignore this variation and take $S_0 = 2500$ l/s.

From Eq. (3) we can see that H is the ratio of the incident flux to an average diffusion flux. For $H \ll 1$ diffusion is unimportant. The pumping speed

is independent of pressure and decreases as the getter fills toward equilibrium with an exponential rate $S_0 P / M q_0$ with M the getter mass. For $H \gg 1$, diffusion will be the rate-limiting step. In this case S decreases with an exponential fall-off σ where

$$\sigma = \alpha D / L^2 \quad (4)$$

and α is a parameter which is of the order of $\pi^2/4$ and depends weakly on H .

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus utilized in the present experiments is shown schematically in Fig. 1. A standard SAES Zr-Al alloy getter module is contained in a stainless steel chamber of 166 l volume, which can also be pumped by a turbomolecular pump with a measured 340 l/s H_2 pumping speed. This pump was valved off during the getter pumping speed measurements. Pressure monitors include an absolute capacitance manometer, two Bayard-Alpert ionization gauges, and a Schultz-Phelps ionization gauge. H_2 gas is introduced through a heated Pd leak followed by a piezo-electric valve, and a calibrated conductance. Differential pressure measurements across this conductance are used to infer the H_2 flow rates. The pressure is feedback stabilized using either the capacitance manometer or one of the Bayard-Alpert gauges.

Prior to a run, the getter was heated resistively to 700°C for at least 45 minutes in order to activate it. The getter was also thermally desorbed such that the H_2 concentration was $\leq 5 \times 10^{-2}$ Torr-l/g. H_2 gas at the desired pressure P was then introduced into the chamber and the gas flow was measured as the initially desorbed getter was loaded to its equilibrium concentration q_0 where

$$q_0 = (P/K)^{1/2} \quad (5)$$

with K the equilibrium constant. In all cases q_0 was less than 10 Torr-l/g. Measurements were made with the getter temperature in the range of 540°C-750°C. These elevated temperatures were chosen to avoid concentrations exceeding the embrittlement limit,⁸ which would otherwise occur at lower temperatures and higher pressures. In their actual use, the getters are typically operated at 400°C, and exposures to higher pressures are limited to times such that embrittlement concentrations are not reached.

IV. RESULTS

Fig. 2 shows the measured H_2 pumping speed S as a function of time t at 540°C for four values of the parameter H calculated from Eq. (3). The corresponding values for P are noted also. S is determined from the measured flow into the getter and from Eq. (2). Also shown in Fig. 2 are the theoretical predictions of S for values of H from 0.1 to 5.0. Within the uncertainties indicated for the experimental H values, good agreement is obtained between theory and experiment for both regimes of $H \ll 1$ and $H \gg 1$. Similar data obtained at 670°C are also in agreement with the predicted behavior.

The predictions in Fig. 2 utilized a previously measured value⁶ for D at 540°C. From the present data over the temperature range of 540°C to 750°C, we have inferred values for D from the exponential slope of the time dependence of S in the large H cases. These values are plotted in Fig. 3. The constant α in Eq. (4) was determined from the numerical solutions of Ref. 5. The fitted curve (shown in Fig. 3) gives

$$D = \exp [-4.0(1.1) - 9100 (450)/T] \text{ cm}^2 \text{ s}^{-1}, \quad (6)$$

with T the temperature in $^{\circ}\text{K}$. This measured diffusivity is in agreement with previous measurements determined from desorption data.⁶

In Fig. 4 the values of S , measured when the getter is loaded to 0.1 and 0.2 of its equilibrium value, are plotted as functions of P for a getter temperature of 670°C . Also plotted are the predicted curves, which are in reasonable agreement. In addition, our data agree well with a previous measurement.⁹ The characteristic behavior of S is that it is pressure independent for $H \lesssim 1$ or $P \lesssim P_D$ where, from Eqs. (3) and (5),

$$P_D \sim \frac{D_p^2 A^2}{K S_o^2 L^2}. \quad (7)$$

For $P \gtrsim P_D$, diffusion into the bulk limits the pumping speed, and $S \sim P^{-1/2}$.

V. SUMMARY

We have measured the pumping speed of Zr-Al for H_2 over the pressure range of 10^{-5} and 10^{-2} Torr and temperature range 540°C - 750°C . We find that our results are in close agreement with the predictions of a theoretical model of bulk getter operation⁵ which includes both surface kinetic processes and bulk diffusion. For $P \lesssim P_D$ [given by Eq. (7)], bulk diffusion is unimportant and S is independent of pressure, while for $P \gtrsim P_D$ diffusion is rate-limiting, and S varies as $P^{-1/2}$. From the high pressure data, we infer values for D which are in good agreement with previous results.⁶

From the close agreement between the predicted and observed behavior found here, we conclude that the theoretical model accurately describes the Zr-Al getter operation. For the normal operating temperature of 400°C ,

$P_D \sim 10^{-3}$ Torr. If it is necessary to operate at greater pressures, the temperature can be increased to raise P_D and consequently maintain the plateau pumping speed.

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FIGURE CAPTIONS

Fig. 1. Schematic of the apparatus utilized for the present measurements.

Fig. 2. Graph of the measured H_2 pumping speed S vs. time for $T=540^\circ\text{C}$ obtained for values of H as noted. The pressures corresponding to these values of H are 9.9×10^{-6} Torr ($H=0.23$); 1.0×10^{-4} Torr ($H=0.73$); 4.1×10^{-4} Torr ($H=1.46$); and 2.8×10^{-3} Torr ($H=3.7$). The getter was initially unloaded. Also shown are the theoretical predictions for various H values.

Fig. 3. Graph of the measured hydrogen diffusivity as a function of $1/T$ for the temperature range 540°C - 750°C . The solid line is at least squares fit.

Fig. 4 Graph of the measured normalized pumping speed S/S_0 as a function of pressure for $T=670^\circ\text{C}$, and loadings of 0.1 and 0.2 of their equilibrium value. Theoretical predictions are shown as solid lines.

Fig. 1

Fig. 2

Fig. 3

Fig. 4