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Hydrogen traps in the outgassing model of a stainless steel vacuum chamber

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This article describes a model for hydrogen outgassing into a stainless steel vacuum chamber. It accounts for the geometry of the chamber components, the hydrogen dissolved in those components, and the processes of diffusion, recombination, and trapping. Strongly bound or "trapped" hydrogen, which occurs at heterogeneities such as dislocations and grain boundaries, can hold most of the dissolved hydrogen even though those locations comprise fewer than 0.1% of all lattice sites. Four simplifications allowed practical use of the model: (1) Each component was described as a one-dimensional object. (2) The hydrogen initially dissolved in each component was described as a uniform concentration. (3) Accurate, consistent values were used to describe diffusion and recombination in stainless steel types 304 and 316 [Grant et al., J. Nucl. Mater. 149, 180 (1987); 152, 139 (1988)]. (4) Only one type of hydrogen trap was considered, and trapping was ignored in components made from vacuum remelted stainless steel. The simple model was developed and validated by comparing it to outgassing measurements. Traps were required to describe the outgassing from a component made of drawn stainless steel 304. The initial hydrogen concentration in that component was comparable to concentrations found elsewhere by thermal desorption and almost 100 times larger than in the components made of vacuum remelted 316 stainless steel. The model’s usefulness was illustrated by using it to predict the outgassing of a vacuum chamber made of type 304 stainless steel. [http://dx.doi.org/10.1116/1.4869962]

I. INTRODUCTION

Hydrogen outgassing often limits the ultimate vacuum in a stainless steel vacuum chamber. In most situations, materials selection, baking, and continuous pumping lead to a satisfactory low pressure, but sometimes the chamber cannot be baked at high temperature or continuous pumping is not possible. Then, it may be useful to understand the outgassing with a model that accounts for the hydrogen dissolved in the chamber components. A sophisticated model would include:

1. a three-dimensional, finite element description of the component geometries
2. the initial hydrogen concentrations as determined by direct analysis of the component alloys
3. diffusion in the steel and recombination at the surface
4. hydrogen trapping.

The present investigation showed that a simple model can be adequate if it accounts for hydrogen trapping. The simplifications were as follows:

1. Each component was described as a one-dimensional object.
2. The initially dissolved hydrogen was described as a uniform concentration.
3. Accurate, consistent values, obtained by Grant et al.,1–3 were used to describe diffusion and recombination in stainless steel types 304 and 316.
4. Only one type of hydrogen trap was considered, and trapping was ignored in components made from vacuum remelted stainless steel.

The simple model was developed and validated by comparing it to outgassing measurements. Traps were required to describe the outgassing from a component made of drawn stainless steel 304. The initial hydrogen concentration in that component was comparable to concentrations found elsewhere by thermal desorption and almost 100 times larger than in the components made of vacuum remelted 316 stainless steel. The model’s usefulness was illustrated by using it to predict the outgassing of a vacuum chamber made of type 304 stainless steel.

Hydrogen outgassing from stainless steel is widely known to be controlled by the diffusion of hydrogen atoms within the steel and their recombination into molecules at the surface.4–7 Less well known is the influence of hydrogen traps, which are sites at which a hydrogen atom has a large binding energy; the sites occur at heterogeneities such as dislocations and grain boundaries. Hydrogen traps comprise a small fraction of all lattice sites, typically less than 0.1%, but they can hold almost all of the hydrogen in commercial stainless steel.

Reviews 8–15 have cited hundreds of studies of hydrogen in steel. Few of those studies were concerned with outgassing into vacuum chambers; more typical motivations were the degradation of tanks and pipes caused by hydrogen embrittlement and the degradation and outgassing of vessels used for nuclear fission and nuclear fusion. The diverse methods used to drive hydrogen into steel have included a large gas pressure (>10 MPa), an electric potential in a

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liquid ionic solution, and implantation by an ion beam. Due to this diversity of motivations and methods, many of the studies are not relevant for understanding low hydrogen pressures in vacuum chambers made of austenitic (AISI series 300) stainless steel. The most relevant studies for understanding vacuum chambers seem to be the measurements of AISI types 304 and 316 made by Grant, Cummings, and Blackburn.1-3 Their results, which are discussed in Appendix A, are key parameters in the present model.

The present model was devised to understand outgassing in a small vacuum chamber that was used to measure vapor pressures near 10 Pa. Hydrogen outgassing was a problem because the chamber (1) operated at temperatures up to 200°C, which greatly increased the outgassing rate, (2) had a large surface-to-volume ratio, and (3) could not be pumped while it was being used to measure vapor pressure. The chamber was baked five times under vacuum to reduce the outgassing rate, which was monitored by occasionally shutting the valve to the pump and observing the rise of pressure with time P(t). As shown in Fig. 1, P(t) for the first bake did not have a simple dependence on time t. This unexpected behavior, observed also in the later bakes, occurred because some components were absorbing the hydrogen while others were outgassing.

The model was used to calculate the curves labeled \( \frac{P_{\text{calc}}}{P_{\text{meas}}} \) in Fig. 1. The model's generality suggests that it would be useful in more typical vacuum chambers.

Figure 1 shows also the nominal outgassing per unit area

\[
\frac{V}{RTA_{\text{total}} \frac{dP_{\text{meas}}}{dt}},
\]

where \( R \) is the universal gas constant, and \( V, T, \) and \( A_{\text{total}} \) are, respectively, the volume, temperature, and total surface area of the chamber. The outgassing per unit area from a specific chamber component might differ by an order of magnitude from this simple estimate.

Section II paper reviews hydrogen traps, and Secs. III–V then describe the model, the apparatus, the outgassing measurements, and a comparison of the model to the measurements. Section VI uses the model to predict the outgassing into a vacuum chamber made of type 304 stainless steel.

II. HYDROGEN TRAPS

A 1973 review of vacuum materials16 mentioned hydrogen traps but dismissed them as an insignificant cause of outgassing. However, later reports of puzzling outgassing from stainless steel questioned whether diffusion and recombination were sufficient explanations. For example, Jousten17 described outgassing of a vacuum chamber that had been vacuum-fired at 1000°C; the outgassing that followed later bake-outs at lower temperatures paradoxically increased with the temperature of the bake-out. Studies by Nemanič and coworkers18-26 of thin-walled chambers and heated stainless steel samples include reports of anomalous outgassing behavior; slow but large outgassing occurred at 800°C,22 and significant redistribution of the hydrogen occurred at room temperature.23

Two reviews of hydrogen in vacuum systems briefly discussed the significance of traps. Redhead5 referred to traps as “multiple diffusion states,” and he noted the observations of multiple peaks in thermal desorption measurements27-30 and in the investigations of Nemanič and coworkers. He called for experimental confirmation of the connection between traps and unexplained hydrogen outgassing. Ishikawa and Nemanič31 emphasized that an outgassing model that includes only diffusion gives large errors, and that adding surface recombination to the model is difficult because the measured coefficients depend greatly on the surface treatment. Traps were first invoked in 1949 by Darken and Smith32 in their paper about diffusion of hydrogen from sulfuric acid into steel. McNabb and Foster33 devised the first model of diffusion that included trapping, and Oriani34 applied that model to experimental data by assuming thermodynamic equilibrium between trapped and untrapped states.

Figure 2 is a simple picture of hydrogen diffusion and trapping in steel. Diffusion occurs because the hydrogen atoms walk randomly between the potential wells of the lattice, which are separated by an energy barrier \( k_BT_{\text{lattice}} \), where \( k_B \) is the Boltzmann constant. Trapping occurs when a hydrogen atom encounters a site with a deeper potential well. A trap is characterized by two energies; entering the trap requires the energy \( k_BT_{\text{entr}} \), and exiting the trap requires the energy \( k_BT_{\text{exit}} \). The two barrier energies and the concentration of traps affect how the concentration of trapped hydrogen changes with time.

In general, the traps in stainless steel will have a distribution of barrier energies. Thermal desorption measurements provide some information about the distribution; for
example, Mizuno et al.\textsuperscript{28} used four values of \(T_{\text{exit}}\) to describe their data. Here, I consider only one type of “reversible” trap and make no speculation about its physical origin. A trap is said to be irreversible if no hydrogen can escape the trap at the measurement temperatures. Appendix B gives details of how traps were used in the present model, which does not assume thermodynamic equilibrium.

III. MODEL

The components of a vacuum chamber can include thin walls, thick flanges, and more complex shapes such as valves. For simplicity, the model describes each component as a one-dimensional solid whose thickness spans the distance between the inside \((x = 0)\) and outside \((x = L)\) surfaces of the vacuum chamber. Although the model allows no transverse diffusion, the component is assigned a cross-section area \(A\) because the flux of hydrogen through the solid is proportional to \(A\). As described in Appendix A, the component is characterized also by the bulk properties of diffusivity \(D\), permeability \(\phi\), and the surface reaction coefficients \(k_1\) and \(k_2\).

Each component is divided into \(N\) elements, and each element contains dissolved hydrogen with a total concentration

\[c_{\text{total}}(x, t) = c(x, t) + c_{\text{trap}}(x, t),\]  

(2)

which depends on position \(x\) and time \(t\). The first and second terms of Eq. (2) are, respectively, the concentrations of untrapped and trapped hydrogen. (All concentrations are in SI units of moles of atomic hydrogen per cubic meter.)

Let us discuss first the untrapped “diffusible” hydrogen. Within the solid, diffusion governs the transport of diffusible hydrogen

\[\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2},\]  

(3)

where \(D\) is the diffusion constant. At the interior surface, the flux of hydrogen from the steel into the chamber is proportional to the square of the concentration at the surface of the solid due to the second-order kinetics of the reaction \(\text{H}_2 = 2\text{H}\) (Sievert’s law). The flux in the opposite direction is driven by the hydrogen partial pressure \(P\) in the chamber. The net molar flux per unit area into the surface layer is

\[J(t) = k_1 P(t) - k_2 [c(0, t)]^2,\]  

(4)

where \(c(0, t)\) is the concentration of diffusible hydrogen at time \(t\) and position \(x = 0\) (element 0). The coefficients \(k_1\) and \(k_2\) are, respectively, the rate constants for dissociation and recombination of hydrogen. The net flux out of the chamber’s exterior wall at \(x = L\) (element \(N\)) has a similar description except that the partial pressure of hydrogen in the surrounding atmosphere can be approximated as zero.

If pumping maintains the chamber pressure at \(P = 0\), outgassing continually removes hydrogen from each component. Without pumping, the hydrogen pressure in the chamber increases at the rate

\[\frac{\partial P}{\partial t} = -\frac{RT}{V} \sum_i A_i J_i,\]  

(5)

where the sum is over all of the chamber components. Equations (4) and (5) allow the fluxes \(J_i(t)\) to affect each other when the pressure is nonzero.

Now let us discuss the trapped hydrogen. As described in Appendix B, the concentration of diffusible hydrogen in each solid element is affected by the local concentration of trapped hydrogen as well as by the diffusion of diffusible hydrogen from adjacent elements. At sufficiently high temperature, the local concentrations of diffusible and trapped hydrogen are in thermodynamic equilibrium, and specifying the temperature and the total concentration \(c_{\text{total}}\) yields the concentration of diffusible hydrogen \(c\) [Eq. (B4)]. At lower temperatures, the two concentrations may not be in equilibrium, and the evolution of \(c(x, t)\) and \(c_{\text{trap}}(x, t)\) is governed by a differential equation [Eq. (B2)].

For the present apparatus, traps were required to represent the component made of stainless steel 304. The traps were included in the simplest way possible by assuming that there was only one type of trap and that the energy barrier to enter the trap was the same as the barrier between ordinary lattice sites, namely, \(T_{\text{enter}} = T_{\text{lattice}}\). With these assumptions, only two trap parameters must be specified: the exit barrier temperature \(T_{\text{exit}}\) and the fraction \(f_{\text{trap}}\) of lattice sites that are traps. (Using \(T_{\text{enter}} = 2T_{\text{lattice}}\) caused only small changes in the results calculated for the present apparatus. However, the calculation for the bake-out of a conventional vacuum chamber at 400 °C, presented in the last section, required such a generalization.)

The model approximates the initial concentration distribution for each component by a constant, \(c_{\text{total}}(x, 0) \equiv c_0\). Ideally, \(c_0\) would be measured by thermal desorption or melt degassing, but knowing how the stainless steel was processed can enable an adequate estimate. See Table I, which lists measurements of the total concentration of hydrogen dissolved in samples of series 300 stainless steel. The samples were processed by various methods, but none
was purified by remelting the steel under vacuum. All but four of the 14 measurements fall in the range of 9 mol m$^{-3}$/C0$^3$ to 33 mol m$^{-3}$/C0$^3$, which also includes the value 22 mol m$^{-3}$/C0$^3$ that described a component in the present apparatus. Thus, a reasonable estimate for stainless steel purified by ordinary methods is $c_0 \approx 20$ mol m$^{-3}$.

A much lower value for $c_0$ is possible if the stainless steel was purified by remelting under vacuum. In Collins' helpful summary of the methods used to purify type 316L, vacuum induction melting (VIM) and vacuum arc melting (VAR) are said to be better for high purity service. As discussed later, the present work found that vacuum valves and fittings made of stainless steel 316L purified by VIM/VAR double melt had an initial concentration of only $c_0 \approx 0.3$ mol m$^{-3}$.

Using more than one component in the model requires a description of the diffusable and trapped hydrogen in each component. Because the components are one-dimensional, they interact with each other only through the chamber pressure; for example, if the chamber pressure is nonzero, component 1 can be outgassing while component 2 is absorbing. Appendix C gives the sequence of calculations that were used to implement the finite element model.

### IV. APPARATUS

Outgassing was measured in three vacuum manifolds, each of which comprised pneumatic valves, thick-walled metal gasket fittings [VCR (Ref. 39)], and two capacitance diaphragm gauges (CDGs) (Figs. 3 and 4).

### V. MEASUREMENTS OF THE CHAMBER PRESSURE

The apparatus was baked five times. The first bake, shown in Fig. 1, was limited to 200 °C and lasted one month. The second bake, shown in Fig. 5, was at 250 °C and lasted one week. The last three bakes, shown in Figs. 6–8, varied the temperature between 30 °C and 250 °C. The manifold was not vented to atmosphere during any of the bakes.
Each figure shows also the nominal outgassing per unit area. Despite some averaging of the data, Figs. 7 and 8 are noisy at small outgassing rates due to the limited stability of the CDGs. Equation (1) was used only to estimate the nominal outgassing, but it was not used in the model that calculated $P_{\text{calc}}$.

During each bake, the pump was frequently closed to observe the resulting increase of pressure. The pressure history $P(t)$ seen during bake 1 (Fig. 1) is typical of all five bakes. Closing the pump caused $P(t)$ to increase as a nonlinear function of time $t$, and the outgassing decreased after each of the pumping cycles. The nonlinear time dependence did not agree with that expected from a leak or from the outgassing of water or hydrocarbons. An attempt to determine the gas species by connecting a residual gas analyzer to the 50 cm$^3$ manifold was unsuccessful due to outgassing from the much larger surface area of the analyzer. Hydrogen was suspected because cooling the sample tube to 77 K caused a pressure decrease that was consistent with ideal gas behavior.

In response to the outgassing seen in manifold 1, the manifold was rebuilt with new valves and new CDGs that could be baked at a higher temperature. Figure 5 shows the pressure measured in manifold 2 during bake 2. In contrast to bake 1, the pressure increases were smaller, and the outgassing was reduced to a satisfactory level in one week instead of one month. The smaller pressure increases were attributed to the absence of a sample tube, and the faster reduction of outgassing was attributed to the higher bake temperature.

Manifold 3 was created by adding a new valve and sample tube to manifold 2. Figure 6 shows the pressure measured during the first bake of manifold 3 (bake 3). The temperature was varied to acquire data that could be used to test the outgassing model. The maximum outgassing rate was five times larger than in manifold 2, apparently due to the presence of the sample tube made from drawn stainless steel 304.

VI. MODELING THE CHAMBER PRESSURE

The chamber was modeled as five components that represented (1) the valve bodies, (2) the CDG bodies, (3) the
VCR fittings, (4) the thin-walled sample tube, and (5) the CDG diaphragms. Figure 9 is a diagram of the model’s geometry.

The model’s fixed parameters included the temperature history \(T(t)\), the pumping history (\(P = 0\) when the chamber was pumped), the material properties (\(D\), \(k_1\), \(k_2\)), and the component dimensions (\(L\), \(A\)). Table II lists the materials and thicknesses of the components. Some of the thicknesses are approximate, either for simplicity (vacuum fittings and CDG bodies) or because the exact value was not available (CDG diaphragms). The values of \(D\), \(k_1\), and \(k_2\) for Inconel and stainless steels 304 and 316 were obtained by extrapolating the formulas in Appendix A to lower temperatures. Values for Monel were not available, so they were assumed to be the same as for Inconel; nickel is the main element in both alloys.

The model assumed that the outgassing of other species, including water, was negligible. Except for the sample tube, this assumption was reasonable for all of the components because they were frequently evacuated at temperatures above 150°C in the normal course of making vapor pressure measurements. It was entirely true for bake 2, which included no sample tube, and bake 5, whose sample tube had not been exposed to atmosphere since the previous bake.

The assumption was likely true also for bake 1, whose sample tube had previously held dodecane; that species would have quickly been removed because it is nonpolar and has a large vapor pressure at 200°C. However, the assumption was likely false at the beginnings of bakes 3 and 4, which used new sample tubes that had been exposed to atmosphere. Even so, Figs. 6 and 7 show that the differences between the measured and calculated pressures during the first day of baking are comparable to the differences seen later.

### A. Using the model without hydrogen traps

The model was applied first to the simplest case, manifold 2, which was baked at a constant temperature and did not include a stainless steel 304 sample tube. The model was fit to the data shown in Fig. 5 by adjusting the initial concentration of hydrogen in each of the components. For simplicity, the initial concentrations were assumed to be uniform \((c(0,x) = c_0)\), and the initial concentration of the CDG diaphragms was set to zero \((c_0 = 0)\). The diaphragms were so thin that their initial concentrations had little influence on the model. These two simplifications were used for all five bakes. The model thus had only three free parameters, namely, the values of \(c_0\) in the valve bodies, the CDG bodies, and the vacuum fittings. Traps were assumed to be absent.

Automated fitting of the free parameters would have been difficult due to the nonlinearity of the model and the complicated time dependences of the temperature and pressure, so the fitting was done by manually adjusting the values of \(c_0\). The resulting fit shown in Fig. 5 reproduces the observed nonlinear time dependence of \(P(t)\) qualitatively for the first day and quantitatively for the following six days. The fitted initial concentrations could be described by the same value for all three components. That value, \(c_0 = 0.26\) mol m\(^{-2}\), is significantly smaller than the concentrations listed in Table I. The valve bodies and the vacuum fittings likely had small initial hydrogen concentrations because they were made of vacuum remelted stainless steel.

### B. Using the model with hydrogen traps

#### 1. Manifold 3

Manifold 3, which comprised manifold 2 plus a sample tube and an additional valve, was baked three times at temperatures that varied between 30°C and 250°C. Figure 6 shows the temperature and pressure histories during bake 3, which followed the addition of the stainless steel 304 sample tube. The maximum pressure of accumulated hydrogen was five times higher than the maximum for manifold 2, which implied that the sample tube released most of the hydrogen.

The data of Fig. 6 could not be described by a model that incorporated only diffusion and surface recombination. Therefore, traps were added to the properties of the stainless steel 304 sample tube. As discussed earlier, only one type of trap was used, and the entrance barrier was assumed to be the same as the lattice barrier, i.e., \(T_{\text{enter}} = T_{\text{lattice}}\). The model for bake 3 then had only three free parameters, all associated with the sample tube: the initial hydrogen concentration \(c_0\),

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Table II: Dimensions and alloys of the components of manifold 1 (volume = 50 cm\(^3\)), manifold 2 (15 cm\(^3\)), and manifold 3 (29 cm\(^3\)). The valves and CDGs in manifold 1 were made by companies different from those that made the valves and CDGs in manifolds 2 and 3. Manifold 2 did not include a thin-walled sample tube.

<table>
<thead>
<tr>
<th>Manifold</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valve bodies</td>
<td>0.6</td>
<td>316L</td>
<td>40</td>
</tr>
<tr>
<td>CDG bodies</td>
<td>0.3</td>
<td>Monel</td>
<td>77</td>
</tr>
<tr>
<td>VCR fittings</td>
<td>0.3</td>
<td>316L remelt</td>
<td>60</td>
</tr>
<tr>
<td>Thin-walled tube</td>
<td>0.05</td>
<td>304</td>
<td>45</td>
</tr>
<tr>
<td>CDG diaphragms</td>
<td>0.02</td>
<td>Inconel</td>
<td>14</td>
</tr>
</tbody>
</table>

---

the trap fraction $f_{\text{traps}}$ and the trap exit barrier temperature $T_{\text{exit}}$. The initial concentrations for the other components were not free because they were set at the values calculated at the end of the previous bake. Approximate agreement with the measurements was obtained by setting $f_{\text{traps}} = 0.015\%$ and $T_{\text{exit}} = 2T_{\text{lattice}} = 13\,200\,\text{K}$. The trap fraction is of the same order of magnitude as that sometimes found by other methods in steel and nickel alloys.\textsuperscript{40–42} The value of $T_{\text{exit}}$ is comparable with values found elsewhere by thermal desorption in stainless steel 304 (8800–22\,000\,K)\textsuperscript{28} and in stainless steel 316 (20\,000\,K).\textsuperscript{30}

Figures 6–8 compare the calculated and measured pressure histories for bakes 3–5. The model for bakes 4 and 5 used the same values of $f_{\text{traps}}$ and $T_{\text{exit}}$ that were used for bake 4, and the initial concentration for each component was set at the value calculated at the end of the previous bake. Bakes 3 and 4 each had one free parameter, the initial concentration $c_0$ of a newly installed sample tube. The value of $c_0$ for bake 4 was smaller than for bakes 1 and 3 even though the sample tubes for all three bakes were made from the same tubing stock. The smaller value likely occurred because the sample tube for bake 4 had already been air baked in a separate oven at 200 °C. Table III lists the initial hydrogen concentrations.

The agreement between $P_{\text{calc}}(t)$ and $P_{\text{meas}}(t)$ for bakes 3–5 is only approximate. Nevertheless, it is remarkable that it was achieved with only four free parameters, all associated with the sample tube. As shown in Fig. 6, the traps act as a reservoir that releases hydrogen to the lattice when the temperature is raised. A more accurate model would require multiple types of traps and a more sophisticated model of the manifold geometry. For example, bakes 3–5 show that increasing the temperature to 250 °C increased the measured outgassing by more than twice the calculated value. This suggests the existence of additional traps with larger binding energies.

2. Manifold 1

The first attempt to model the data for manifold 1 (Fig. 1), which assigned to the sample tube the same values of $c_0$, $f_{\text{traps}}$, and $T_{\text{exit}}$ that were used for bake 3, was not successful. The second attempt added traps to the description of the Monel CDG bodies; the traps had the same value of $T_{\text{exit}}$ as the sample tube but a larger trap fraction of $f_{\text{traps}} = 0.03\%$.

<table>
<thead>
<tr>
<th>Bake</th>
<th>Manifold</th>
<th>Valve bodies</th>
<th>CDG bodies</th>
<th>Vacuum fittings</th>
<th>Sample tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.0</td>
<td>25</td>
<td>0.26</td>
<td>22</td>
</tr>
<tr>
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<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
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</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.127</td>
<td>0.042</td>
<td>0.042</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0.080</td>
<td>0.037</td>
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<td>12</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0.061</td>
<td>0.038</td>
<td>0.038</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The result, shown in Fig. 1, fails to describe the unusual linearity of the last five pressure cycles but otherwise is in approximate agreement with the measurements.

C. Applying the model to a typical vacuum chamber

The model was used to calculate the outgassing of a vacuum chamber with 3 mm thick chamber walls made of type 304 stainless steel. Most of the calculations were for a bake-out at 400 °C. Prolonged baking at higher temperatures can cause carbide precipitation at grain boundaries, thereby depleting chromium from the alloy.\textsuperscript{29,43}

The calculations presented in this section were simpler than those used for the present apparatus because they included only one component and the hydrogen pressure in the chamber was fixed at zero.

Figures 10 and 11 show the hydrogen distribution in the steel wall while baking the chamber at 200 °C and 400 °C. Calculations are shown with and without traps; the trap fraction, $f_{\text{traps}} = 0.01\%$, and the trap barrier temperature, $T_{\text{exit}} = T_{\text{lattice}} = 6600\,\text{K}$, were similar to those found in the present apparatus. The evolution of the hydrogen distribution without traps resembles that of simple diffusion except that recombination keeps the boundary concentrations above zero; similar plots were first published by Moore.\textsuperscript{44} Adding traps slows the evolution further by an order of magnitude.

Figure 12 shows the outgassing predicted during and after a bake-out at 400 °C. The calculations with traps used a barrier temperature $T_{\text{enter}} = 13\,400\,\text{K}$ as well as the value $T_{\text{enter}} = T_{\text{lattice}} = 6600\,\text{K}$ that described the apparatus. Both calculations used the same difference $\Delta T = T_{\text{exit}} - T_{\text{enter}}$ that determines the equilibrium ratio of trapped and diffusable hydrogen. (The outgassing calculated for the present apparatus was not sensitive to the value of $T_{\text{enter}}$, because it was baked at only 250 °C.)

![Graph](image-url)
The presence of traps had two effects: it slowed the depletion of hydrogen during the bake-out, but it also decreased the outgassing that occurred afterwards at room temperature. The decrease occurred because most of the hydrogen that was freed during the bake-out was retrapped at room temperature. The amount of retrapping depends on the height of the trap entrance barrier $T_{\text{enter}}$. Figure 12 shows that using the nominal value $T_{\text{enter}} \approx T_{\text{lattice}}$ predicts an unrealistically small outgassing rate, while using $T_{\text{enter}} \approx 2T_{\text{lattice}}$ predicts a rate that is consistent with the observed in typical vacuum chambers. The review by Ishikawa and Nemanic$^{31}$ lists rates in the range from $1 \times 10^{-16}$ mol H$_2$ m$^{-2}$ s$^{-1}$ to $2 \times 10^{-12}$ mol H$_2$ m$^{-2}$ s$^{-1}$. (1 mol H$_2$ m$^{-2}$ s$^{-1}$ = 2.5 mbar L s$^{-1}$ cm$^{-2}$.)

Figure 12 suggests that traps will limit the room-temperature outgassing of a vacuum chamber that is made of a stainless steel with a large concentration of traps, such as rolled AISI 304. In this example, baking for only a few hours reduced the hydrogen concentration below the trap concentration, $c_{\text{traps}} = \frac{f_{\text{traps}} c_{\text{Fe}}}{1 - f_{\text{traps}}} = 14$ mol m$^{-3}$, which allowed the traps to act as a getter for hydrogen at room temperature. The retrapping can occur only if the chamber is cooled to room temperature at a sufficiently slow rate. (Appendix B discusses the characteristic trap entry time.) This usually occurs in practice because other considerations, such as differential contraction, limit the cooling rate to less than 1 K min$^{-1}$.

Figure 13 shows the calculated effects of traps and surface cleaning on the room-temperature outgassing as a function of bake-out duration. Grant et al.$^1$ found that cleaning their sample in situ with a hydrogen ion beam increased the recombination rate by a factor of 100, and their corresponding value of $k_1$ was used in the cleaned-surface calculation. (All other calculations used the values of $k_1$ that Grant et al. obtained for samples with an oxidized surface.) For a 400°C bake-out, combining traps and a cleaned surface predicts a room-temperature outgassing that is well below the range observed elsewhere.$^{31}$ It is unclear whether this discrepancy is due to the model or to the difficulty of creating a surface as clean as the ion-milled surface used by Grant et al.

Bernardini et al.$^29$ found that electrochemically cleaning the surface of their samples did not affect their thermal desorption measurements. Their desorption rates may have been limited by traps instead of recombination. Another possibility is that the cleaning itself may have added hydrogen. Under some conditions, point defect clusters and voids could occur at the surface and then trap hydrogen and retard desorption.$^{35}$

The model requires an estimate of the initial hydrogen concentration $c_0$. Fortunately, as illustrated in Fig. 14, the effect of $c_0$ on a bake-out calculation is small. Figure 14 shows the calculated room-temperature outgassing following a 72 h bake-out at 400°C. Although the calculation covers a wide range of $c_0$, the initial concentration in ordinary stainless steel is unlikely to be below the trap concentration, which for a trap fraction of 0.01% is 14 mol m$^{-3}$. Above that concentration, the dependence on $c_0$ is weak, and a suitable estimate suggested by Table I is $c_0 = 20$ mol m$^{-3}$.

![Fig. 11.](image1.png) **Fig. 11.** (Color online) Hydrogen distributions calculated at 400°C, with and without traps, for a continuously pumped vacuum chamber with 3 mm thick walls made of type 304 stainless steel.

![Fig. 12.](image2.png) **Fig. 12.** (Color online) Outgassing calculated for a 400°C bake-out of a vacuum chamber with 3 mm walls of type 304 stainless steel. The initial hydrogen concentration, 20 mol m$^{-3}$, was similar to that found in the present apparatus. The chamber was baked for 72 h and then cooled to 1 K min$^{-1}$ to room temperature. The height $k_1 T_{\text{enter}}$ of the barrier for hydrogen to re-enter a trap strongly affected the outgassing at room temperature. The range of values observed elsewhere comes from the review by Ishikawa and Nemanic (Ref. 31).

![Fig. 13.](image3.png) **Fig. 13.** (Color online) Calculated effects of traps and surface cleaning on the room-temperature outgassing as a function of bake-out duration. The chamber walls were 3 mm type 304 stainless steel with an initial hydrogen concentration of 20 mol m$^{-3}$.
Hydrogen outgassing is usually measured by observing the rate of pressure rise \( dP/dt \) in the absence of pumping. Typically, \( dP/dt \) is constant at room temperature, which is in contrast to the present measurements that found \( P(t) \) to be nonlinear in time at elevated temperatures. In particular, Jousten 46 made careful measurements of \( P(t) \) in a vacuum-fired chamber made of type 316LN stainless steel, 46 and, because \( dP/dt \) was constant, he questioned whether readsoption of hydrogen was significant. This question was revisited by using the present model to calculate the outgassing at 25 °C. The chamber was assumed to be made of type 316 stainless steel with no traps and having 0.1 m \(^3\) volume, 1 m \(^2\) wall area, and 3 mm wall thickness. The initial hydrogen distribution \( c(t,0) \) was created by evolving the model at 300 °C until the maximum concentration in the middle of the wall decreased to a specified value \( c_{\text{max}} \) and then “freezing” the resulting parabolic profile by lowering the temperature to 25 °C. For \( c_{\text{max}} < 0.02 \text{ mol m}^{-3} \), the outgassing calculated at 25 °C was constant in time and proportional to \( c_{\text{max}} \). In particular, \( c_{\text{max}} = 0.01 \text{ mol m}^{-3} \) gave \( dP/dt = 2 \times 10^{-8} \text{ Pa s}^{-1} \), similar to the rate reported by Jousten. The corresponding outgassing per unit area, \( 1 \times 10^{-13} \text{ mol H}_2 \text{ m}^{-2} \text{ s}^{-1} \), is comparable to that observed elsewhere. A reasonable question is why the concentration after vacuum firing was even as large as \( 0.01 \text{ mol m}^{-3} \). A possible answer is the influence of atmospheric hydrogen, which has a partial pressure of \( P_{\text{atm}} = 0.05 \text{ Pa} \). At 300 °C, the time constant for equilibration of diffusion in 3 mm of type 316 stainless steel is less than one day, and the equilibrium concentration is
\[
c_{\text{total}} = \frac{\phi P_{\text{atm}}^{1/2}}{D} = 0.009 \text{ mol m}^{-3}.
\]

Vacuum firing is done at approximately 1000 °C, and its effect on the number and type of hydrogen traps is unclear. Adding 0.01% traps to the model decreased the outgassing rate far below the observed rate, even with \( c_{\text{max}} \) as large as 1 mol m \(^{-3}\).

VI. SUMMARY AND CONCLUSIONS

This article presented a simple model that can describe the hydrogen outgassing in a stainless steel vacuum chamber by accounting for hydrogen trapping as well as diffusion in the steel and recombination at the surface. Useful simplifications of the model include:

1. Describing each component of the chamber as a one-dimensional object.
2. Describing the initially dissolved hydrogen as a uniform concentration.
3. Using accurate, consistent values \(^{1–3}\) to describe diffusion and recombination in stainless steel types 304 and 316.
4. Considering only one type of hydrogen trap, and ignoring trapping in components made from vacuum remelted stainless steel.

The model was validated by comparing it to the outgassing measured in a small vacuum chamber that was heated to temperatures up to 250 °C. Hydrogen traps were required to describe the outgassing from a chamber component made of drawn stainless steel 304. The initial hydrogen concentration in that component was comparable to concentrations found elsewhere by thermal desorption and almost 100 times larger than in the components made of vacuum remelted 316 stainless steel. The model’s usefulness was illustrated by using it to predict the outgassing of a vacuum chamber made of type 304 stainless steel.

The model allows one to estimate the effects of geometry, stainless steel type, and surface cleaning. The latter two variables strongly influence the surface reaction coefficients; the value of \( k_1 \) for type 316 is about 10 times larger than for type 304, and using ion beam milling to remove the oxide layer from type 304 increases \( k_1 \) by a factor of 10\(^3\). This investigation did not attempt to estimate the effect of vacuum firing a chamber at 1000 °C because Grant, Cummings, and Blackburn \(^{1–3} \) measured the relevant material properties up to only 700 °C. Extrapolating their results to much higher temperatures might not be reliable.

The following points are useful to remember when trying to reduce hydrogen outgassing.

1. Most of the hydrogen dissolved in type 304 stainless steel, and perhaps other types, can reside in traps with binding energies larger than the activation energy of diffusion. Increasing the temperature will then release hydrogen and cause the outgassing rate to increase beyond that predicted by the temperature dependences of diffusion and recombination.

2. The concentration of hydrogen in a component made from a stainless steel containing traps, say rolled type 304 stainless steel, may be 100 times greater than in a component made from stainless steel that was purified by remelting under vacuum.

3. Due to hydrogen’s partial pressure of 0.05 Pa in air, the hydrogen dissolved in a stainless steel component cannot be reduced to an arbitrarily low concentration by heating the component in air.

Future investigations of hydrogen trapping in stainless steels could go in several useful directions. First, the measurement method used here could be improved by building an apparatus specifically to measure hydrogen outgassing. A spinning rotor gauge would enable useful measurements...
down to 10 μPa. Even though the gauge easily would have to be at room temperature, the present model easily allows different apparatus components to be at different temperatures. Second, the present 1D model could be incorporated into a 3D multiphysics model. Third, thermal desorption measurements of hydrogen concentration in stainless steel samples could be improved by taking data at several temperatures and fitting the data to a model with only a few types of traps, as was done by Mizuno et al. The present model might help account for adsorption by the walls of the desorption apparatus. Finally, the method of Grant, Cummings, and Blackburn could be revived and improved to measure \( D, \phi \), and \( k_1 \) for more materials, more surfaces, and over a wider range of temperature.

**ACKNOWLEDGMENTS**

The author thanks Walt Bowers and Jeff Kelley for constructing parts of the apparatus, and he is grateful for helpful discussions with Richard Ricker, Michal Fulem, Kvetoslav Růžička, Rai Weiss, Tom Lucatorto, Doug Olson, and Pat Abbott. This work was funded in part by the NIST Office of Microelectronic Programs.

**APPENDIX A: DIFFUSIVITY \( D \), PERMEABILITY \( \phi \), AND SURFACE REACTION COEFFICIENTS \( k_1, k_2 \)**

Tables IV–VI reproduce from the literature the measured coefficients that were used in the present work. They describe diffusivity \( D \), permeability \( \phi \), and the surface reaction coefficient for dissociation \( k_1 \). The coefficient for recombination \( k_2 \) is derived from these three quantities by

\[
k_2 = k_1 \left( \frac{D}{\phi} \right)^2.
\]

Table IV gives also the temperature ranges in which \( D, \phi \), and \( k_1 \) were measured. Arrhenius temperature dependences accurately describe the coefficients within those ranges, which suggest that they can be extrapolated reliably to the temperature range used in the present work.

The diffusion of hydrogen in iron and steel has been measured many times and in many ways; a 1983 review of iron cites more than 30 studies. See also the reviews by Volk and Alfeld and by LeClaire. The best values for stainless steels 304 and 316 are those measured by Grant, Cummings, and Blackburn. They oscillated the hydrogen pressure on one side of a metal membrane, measured the resulting oscillatory flow from the other side, and applied an elegant data analysis (which assumed no traps) that yielded simultaneous values for the diffusivity, permeability, and surface reaction coefficients. Their results are likely the most accurate because their method had the following advantages:

1. The driving pressures were much smaller than the MPa pressures used in other studies to “charge” steel samples, so the measurement conditions were more relevant to the problem of hydrogen outgassing.

2. The analysis yielded self-consistent values for the three relevant properties \( D, \phi \), and \( k_1 \). In contrast, most studies used less direct methods that yielded values for only one or two of these properties. An example is coating the sample with palladium to suppress the barrier caused by surface reaction.

3. Fourier analysis of the oscillating gas flow prevented errors caused by stray outgassing. The method was validated by demonstrating that changing the driving frequency from 0.1 Hz to 0.6 Hz gave consistent results.

4. The effect of surface preparation on the surface reaction coefficients was investigated by using an ion beam to clean the sample’s oxidized surface \( \text{in situ} \). The cleaning increased \( k_1 \) but had no effect on \( D \) and \( \phi \).

Note that the microstructure of a thin membrane can differ from that of a thick sample, and that such a difference might affect both the solubility and the effective diffusivity.

The Inconel values are those obtained by Esteban et al. Their analysis yielded values for \( \phi \) and \( k_1 \) as well as \( D \), but their constant pressure technique did not share all of the above advantages.

It is useful to review the relationships among \( D, \phi, k_1 \), and \( k_2 \), which sometimes can seem obscure, especially when non-SI units are used. Ignore traps and imagine the steady state depicted in Fig. 15, in which molecules of hydrogen gas at pressure \( P \) dissociate into atoms at the surface \( (x = 0) \) of a steel membrane of thickness \( L \), diffuse through the membrane,

### Table IV. Coefficients that describe diffusivity, \( D(T) = D_0e^{\exp(-T/T_k)} \). Also listed are the temperature ranges in which \( D, \phi \), and \( k_1 \) were measured.

<table>
<thead>
<tr>
<th>Material</th>
<th>( T ) range (K)</th>
<th>( D_0 ) (m(^2) s(^{-1}))</th>
<th>( T_k ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>Ref. 1</td>
<td>645–965 (1.22 ± 0.06) \times 10(^{-6})</td>
<td>6600 ± 50</td>
</tr>
<tr>
<td>316</td>
<td>Ref. 2</td>
<td>502–863 (7.3 ± 0.9) \times 10(^{-7})</td>
<td>6300 ± 110</td>
</tr>
<tr>
<td>Inconel 800</td>
<td>Ref. 49</td>
<td>427–780 (3.87 ± 10(^{-7}))</td>
<td>5749</td>
</tr>
</tbody>
</table>

### Table V. Coefficients that describe permeability, \( \phi(T) = \phi_0e^{\exp(-T/T_k)} \).

<table>
<thead>
<tr>
<th>Material</th>
<th>( \phi_0 ) (mol s(^{-1}) m(^{-1}) Pa(^{-1/2}))</th>
<th>( T_k ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>Ref. 1</td>
<td>(4.8 ± 0.2) \times 10(^{-7})</td>
</tr>
<tr>
<td>316</td>
<td>Ref. 2</td>
<td>(8.1 ± 0.7) \times 10(^{-7})</td>
</tr>
<tr>
<td>Inconel 800</td>
<td>Ref. 49</td>
<td>3.94 \times 10(^{-9})</td>
</tr>
</tbody>
</table>

### Table VI. Coefficients used to describe the surface reaction coefficient, \( k_1(T) = k_{10}e^{\exp(-T/T_k)} \). Except where noted, the present model used oxidized values for the stainless steels, and cleaned values for Inconel.

<table>
<thead>
<tr>
<th>Material</th>
<th>( k_{10} ) (cleaned) (mol s(^{-1}) m(^{-2}) Pa(^{-1}))</th>
<th>( T_{k1} ) (cleaned) (K)</th>
<th>( k_{10} ) (oxidized) (mol s(^{-1}) m(^{-2}) Pa(^{-1}))</th>
<th>( T_{k1} ) (oxidized) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>Ref. 1</td>
<td>(1.13 ± 0.10) \times 10(^{-2})</td>
<td>9320 ± 80</td>
<td>(1.43 ± 0.11) \times 10(^{-3})</td>
</tr>
<tr>
<td>316</td>
<td>Ref. 2</td>
<td>(3.2 ± 0.3) \times 10(^{-2})</td>
<td>9710 ± 100</td>
<td>(1.3 ± 0.3) \times 10(^{-4})</td>
</tr>
<tr>
<td>Inconel 800</td>
<td>Ref. 49</td>
<td>2.67 \times 10(^{-10})</td>
<td>4823</td>
<td>4.14 \times 10(^{-6})</td>
</tr>
</tbody>
</table>

and recombine into molecules at the other surface at \( x = L \). In general, dissociation and recombination can occur simultaneously at a surface, as indicated by the equation

\[
\text{H}_2(\text{gas}) \xrightarrow{k_1 P} 2\text{H}(\text{solid solution}).
\]

(A2)

Here \( k_1 \) and \( k_2 \) are, respectively, the rate constants for dissociation and recombination. In steady state, the flux per unit area through the steel

\[
J = D \frac{c(0) - c(L)}{L}
\]

is the same as the flux at the surfaces. For the left surface,

\[
J = k_1 P - k_2 |c(0)|^2.
\]

(A4)

The dependence of \( J \) on the square of the surface concentration, which is known as Sievert’s law, is caused by the second-order kinetics of Eq. (A2). In the special case of equilibrium, \( J = 0 \) and the concentration at \( x = 0 \) is

\[
c(0) = K_s P^{1/2},
\]

where \( K_s = (k_1/k_2)^{1/2} \) is Sievert’s constant. If the pressure at \( x = L \) is zero, the assumption that both surfaces are close to equilibrium transforms Eq. (A3) to

\[
J = \phi P^{1/2}/L,
\]

(A6)

where \( \phi = D K_S \) is the permeation constant.

**APPENDIX B: HYDROGEN TRAPS**

Figure 2 is a simple picture of hydrogen diffusion and trapping in steel.\(^{28}\) Diffusion occurs because the hydrogen atoms walk randomly between the lattice’s potential wells, which are separated by a lattice distance \( x_{\text{lattice}} \) and an energy barrier \( k_B T_{\text{lattice}} \), where \( k_B \) is the Boltzmann constant. There is negligible interaction between hydrogen atoms because the concentrations typical for commercial stainless steel are less than 0.1\%. The resulting rate of diffusion is approximately\(^{31}\)

\[
D = x_{\text{lattice}}^2 \nu e^{-T_{\text{tane}}/T} = D_0 e^{-T_{\text{tane}}/T},
\]

(B1)

where \( \nu \approx 10^{13} \text{ s}^{-1} \) is the typical vibration frequency of a hydrogen atom in a potential well.

Trapping occurs when a hydrogen atom encounters a site with a deeper potential well. A trap is characterized by two energies; entering the trap requires the energy \( k_B T_{\text{enter}} \) and exiting the trap requires the energy \( k_B T_{\text{exit}} \). The two barrier energies and the concentration of traps affect how the concentration of trapped hydrogen changes with time. In equilibrium, the ratio of trapped hydrogen to diffusible hydrogen depends only on the difference \( \Delta T = T_{\text{exit}} - T_{\text{enter}} \). The governing differential equation is

\[
\frac{\partial c_{\text{trapH}}}{\partial t} = \nu e^{-T_{\text{enter}}/T} \left( \frac{c}{c_{\text{Fe}}} \right) \left( 1 - \frac{c_{\text{trapH}}}{c_{\text{traps}}} \right) c_{\text{traps}}
\]

- \( \nu e^{-T_{\text{exit}}/T} \left( \frac{c_{\text{trapH}}}{c_{\text{traps}}} \right) \left( 1 - \frac{c}{c_{\text{Fe}}} \right) c_{\text{traps}},
\]

(B2)

where \( c, c_{\text{trapH}}, \) and \( c_{\text{traps}} \) are, respectively, the concentrations, in mol m\(^{-3}\), of diffusible hydrogen, trapped hydrogen, and traps. For simplicity, the concentration of lattice sites in steel alloys is approximated by the concentration of pure iron, \( c_{\text{Fe}} = 1.4 \times 10^5 \text{ mol m}^{-3} \). The concentration of trapped hydrogen depends on time, while the concentration of traps, \( c_{\text{traps}} = f_{\text{traps}} c_{\text{Fe}} \), is fixed because it is a property of the steel. This equation is similar to the model used by Wilson and Baskes\(^{32,53}\) to describe thermal desorption, but it is generalized by allowing \( T_{\text{enter}} \neq T_{\text{lattice}} \) and it ignores diffusion, which is incorporated elsewhere in the model.

The first term of Eq. (B2) is the rate of change due to atoms entering the traps. It is proportional to both the fraction of lattice sites that are occupied by an untrapped hydrogen atom, \( (c/c_{\text{Fe}}) \), and the fraction of traps that are empty, \( (1 - c_{\text{trapH}}/c_{\text{traps}}) \). Similar reasoning leads to the second term of Eq. (B2), which accounts for atoms leaving the traps. It is proportional to both the fraction of traps that are occupied by a hydrogen atom, \( (c_{\text{trapH}}/c_{\text{traps}}) \), and the fraction of lattice sites that are empty \( (1 - c/c_{\text{Fe}}) \).

The concentration of hydrogen is always small \( (c/c_{\text{Fe}} < 0.001 \), see Table I), which allows Eq. (B2) to be approximated as

\[
\frac{\partial c_{\text{trapH}}}{\partial t} \approx \nu e^{-T_{\text{enter}}/T} c_{\text{traps}}
\]

\[
\times \left[ \left( \frac{c}{c_{\text{Fe}}} \right) \left( 1 - \frac{c_{\text{trapH}}}{c_{\text{traps}}} \right) - e^{-\Delta T/T} \left( \frac{c_{\text{trapH}}}{c_{\text{traps}}} \right) \right],
\]

(B3)

where \( \Delta T \equiv T_{\text{exit}} - T_{\text{enter}} \) is the energy difference between a trap site and a lattice site. In thermodynamic equilibrium, \( \partial c_{\text{trapH}}/\partial t = 0 \), and the fraction of traps that are occupied is\(^{40}\)
The characteristic time for hydrogen to enter the traps is given by
\[
\tau_{\text{enter}} = \frac{c}{c_{\text{traps}}} + e^{-\Delta T/T}.
\]

(Eq. (B4))

Combining Eqs. (B4) and (B5) yields an expression for the equilibrium concentration of diffusible hydrogen \(c\) in terms of the concentrations \(c_{\text{traps}}\) and \(c_{\text{total}}\):
\[
\left(\frac{c}{c_{\text{Fe}}}\right)_{\text{equiv}} = \frac{1}{2} \left[ \left( \frac{c_{\text{traps}}}{c_{\text{Fe}}} + e^{-\Delta T/T} - \frac{c_{\text{total}}}{c_{\text{Fe}}} \right)^2 
+ 4 \frac{c_{\text{total}}}{c_{\text{Fe}}} e^{-\Delta T/T} \right]^{1/2}.
\]

(Eq. (B6))

Equation (B6) cannot be approximated by a simpler expression that is accurate over the full range of expected temperatures and concentrations.

Thermodynamic equilibrium applies at times longer than the characteristic times for hydrogen to enter (\(\tau_{\text{enter}}\)) and exit (\(\tau_{\text{exit}}\)) the traps. Examining the first term of Eq. (B2) shows that the characteristic time for hydrogen to enter the traps is given by
\[
\frac{1}{\tau_{\text{enter}}} = \frac{1}{c_{\text{traps}}} \left( \frac{\partial c_{\text{traps}}}{\partial t} \right)_{\text{enter}}
= \nu e^{-T_{\text{exit}}/T} \frac{c}{c_{\text{Fe}}} \left( 1 - \frac{c_{\text{traps}}}{c_{\text{Fe}}} \right) \leq \nu e^{-T_{\text{exit}}/T} \frac{c}{c_{\text{Fe}}},
\]

(Eq. (B7))

Similarly, the characteristic time for hydrogen to exit the traps is given by
\[
\frac{1}{\tau_{\text{exit}}} = \frac{1}{c_{\text{traps}}} \left( \frac{\partial c_{\text{traps}}}{\partial t} \right)_{\text{exit}}
= \nu e^{-T_{\text{exit}}/T} \frac{c_{\text{traps}}}{c_{\text{Fe}}} \left( 1 - \frac{c}{c_{\text{Fe}}} \right) \leq \nu e^{-T_{\text{exit}}/T}.
\]

(Eq. (B8))

Figure 16 shows that \(\tau_{\text{enter}}\) and \(\tau_{\text{exit}}\) have strong temperature dependences. For example, at a hydrogen concentration of 1 mol m\(^{-3}\), the value of \(\tau_{\text{enter}}\) at 400 °C is small
\[
\tau_{\text{enter}} \geq \left\{ \left(10^{13}\text{s}^{-1}\right) \exp\left[\frac{(-13400\text{ K})}{(673\text{ K})}\right]\right\}^{-1} = 6\text{ s},
\]

but at 25 °C, it exceeds \(10^4\) years.

APPENDIX C: NUMERICAL CALCULATIONS

The finite-element model was implemented in a spreadsheet scripting language (Microsoft VBA\textsuperscript{9}). For most calculations, space intervals of \(\Delta x = 0.06\text{ mm}\) and time steps of \(\Delta t = 10\text{ s}\) were adequate. However, calculations at 400 °C that used the coefficients for cleaned stainless steel caused fast changes that required time steps as small as 0.2 s. The calculation proceeded according to the following pseudocode:

For Component = 1 to 5
Input material, thickness \(L\), cross section area \(A\)
Input trap fraction \(f_{\text{traps}}\), barrier temperatures \(T_{\text{enter}}, T_{\text{exit}}\)
Input initial total distribution of hydrogen \(c_{\text{total}}(x,0)\)
Next Component

For \(t = \text{Start to Stop, step } \Delta t\)
Input temperature \(T(t)\)
For Component = 1 to 5
Calculate temperature dependent properties \(D, k_1, k_2\)
For \(x = 0 \text{ to } L, \text{ step } \Delta x\)
Calculate free hydrogen \(c(x,t)\) from \(c_{\text{total}}(x,t)\) and \(T(t)\) [Eq. (B3) or (B6)]
Next \(x\)
At \(x = 0 \text{ (interior surface)}\)
Calculate outgas flux and update \(c(0,t)\) [Eq. (4)]
Is chamber being pumped?
Yes: Chamber pressure \(P(t) = 0\)
No: Calculate increase of \(P(t)\) due to flux [Eq. (5)]
At \(x = L \text{ (exterior surface)}\)
Calculate outgas flux and update \(c(L,t)\)
For \(x = 0 \text{ to } L, \text{ step } \Delta x\)
Calculate change \(\Delta c(x,t)\) due to diffusion from adjacent \(x\) [Eq. (3)]
Next \(x\)
For \(x = 0 \text{ to } L, \text{ step } \Delta x\)
Increase \(c_{\text{total}}(x,t)\) to \(c_{\text{total}}(x,t) + \Delta c(x,t)\)
Next \(x\)
Next Component
Next \(t\)

\cite{1D. M. Grant, D. L. Cummings, and D. A. Blackburn, J. Nucl. Mater. 149, 180 (1987).}
\cite{2D. M. Grant, D. L. Cummings, and D. A. Blackburn, J. Nucl. Mater. 152, 139 (1988).}
\cite{3D. M. Grant, D. L. Cummings, and D. A. Blackburn, Z. Physikalische Chemie Neue Folge 164, 1585 (1989).}

\begin{figure}[ht]
\centering
\includegraphics[width=0.5\textwidth]{figure16.png}
\caption{(Color online) Minimum characteristic time, in seconds, for a hydrogen atom to enter a trap (\(\tau_{\text{enter}}\)) and to exit a trap (\(\tau_{\text{exit}}\)).}
\end{figure}