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Citation: *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **35**, 041601 (2017); doi: 10.1116/1.4983211

View online: <http://dx.doi.org/10.1116/1.4983211>

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Investigations of medium-temperature heat treatments to achieve low outgassing rates in stainless steel ultrahigh vacuum chambers

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(Received 7 February 2017; accepted 27 April 2017; published 9 May 2017)

The authors investigated the outgassing rates and fluxes of vacuum chambers constructed from common 304L stainless steel vacuum components and subjected to heat treatments. Our goal was to obtain H₂ outgassing flux on the order of 10⁻¹¹ Pa l s⁻¹ cm⁻² or better from standard stainless steel vacuum components readily available from a variety of manufacturers. The authors found that a medium-temperature bake in the range of 400 to 450 °C, performed with the interior of the chamber under vacuum, was sufficient to produce the desired outgassing flux. The authors also found that identical vacuum components baked in air at the same temperature for the same amount of time did not produce the same low outgassing flux. In that case, the H₂ outgassing flux was lower than that of a stainless-steel chamber with no heat treatment, but was still approximately 1 order of magnitude higher than that of the medium-temperature vacuum-bake. Additionally, the authors took the chamber that was subjected to the medium-temperature vacuum heat treatment and performed a 24-h air bake at 430 °C. This additional heat treatment lowered the outgassing rate by nearly a factor of two, which strongly suggests that the air-bake created an oxide layer which reduced the hydrogen recombination rate on the surface. [<http://dx.doi.org/10.1116/1.4983211>]

I. INTRODUCTION

Stainless steels of 304 and 316 series are the most commonly used materials for the construction of vacuum chambers designed to operate in the ultrahigh vacuum and extreme-high vacuum (below 10⁻⁵ Pa, UHV, and below 10⁻⁹ Pa, XHV, respectively¹). The ultimate pressure that can be achieved in a vacuum system is determined by the outgassing rate of the vacuum chamber versus the rate at which gas is removed or the pumping speed. It is well known that hydrogen gas dissolved in the stainless steel during production is the largest contributor to the outgassing rate of stainless steel in the UHV and XHV.^{2,3} Reducing hydrogen outgassing is of paramount importance to achieving UHV and XHV pressures in stainless steel vacuum systems, and is especially important in applications where the pumping speed is small. Dynamic expansion systems, for example, are widely used in vacuum metrology applications to produce a known pressure rise upstream of an orifice of known dimensions in a vacuum chamber, but the pumping speed of these systems is limited to that of the orifice, which is typically tens of liters per second.⁴ Consequently, for typically sized dynamic expansion vacuum chambers with areas on the order of 1000 cm², the outgassing flux (outgassing rate per unit area) must be on the order of 10⁻¹¹ Pa l s⁻¹ cm⁻² to achieve an ultimate pressure in the XHV (1 Pa l s⁻¹ cm⁻² = 10 Pa m s⁻¹). Most users of UHV and XHV systems employ a heat treatment to lower the hydrogen outgassing to achieve a flux in the range of 10⁻¹⁰ to 10⁻¹² Pa l s⁻¹ cm⁻². Three types of baking schemes are commonly employed to degas hydrogen from stainless steel: Vacuum firing, in which the entire vacuum chamber is placed in a vacuum furnace operating at >950 °C and pressures below 10⁻³ Pa;^{2,5-9} medium heat treatment vacuum bake, in which

the vacuum chamber is evacuated and heated to 400–500 °C, typically with the outside of the chamber in air at atmospheric pressure;¹⁰⁻¹³ and a medium heat treatment air-bake, in which the vacuum chamber is baked entirely in air at atmospheric pressure at a temperature of 400 °C or greater.^{6,7,13,14} Hydrogen diffuses through stainless steel as atomic H,^{15,16} and the diffusion coefficient for hydrogen in stainless steel depends exponentially on temperature;¹⁷ increasing the temperature greatly decreases the time it takes for the hydrogen to migrate from the stainless steel bulk to the surface, where it recombines to form H₂ and desorbs from the surface.¹⁸ The time it takes to remove most of the hydrogen from the stainless steel bulk depends on the temperature and material thickness. For most vacuum chambers, vacuum firing is typically done on the order of hours; medium temperature vacuum and air-bakes typically take several days to several weeks. Air-bakes result in the formation of visible oxide layers on the steel surface which have a different diffusion coefficient than the bulk steel in addition to a different surface hydrogen recombination rate.¹⁷ The oxide layers are mostly iron oxide, compared to chromium oxide which dominates the surfaces of unbaked steel.¹⁹ Some have observed that oxide layers can act as diffusion barrier to hydrogen^{2,18-20} and, consequently, can lower the hydrogen outgassing rate. On the other hand, the oxide layers produced by baking have been also observed to change the surface reaction rate,¹⁶ and may also reduce the number of desorption sites. Our results, presented in this paper, support the conclusion that the additional oxide layer reduces hydrogen desorption, but is also consistent with the hypothesis that the oxide layers have a slower diffusion coefficient than bulk steel.

A wide variety of outgassing rates and fluxes for stainless steel can be found in the literature, often making direct comparison among various techniques difficult. Many variables may account for these differences. Surface conditions

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(roughness, welds, contamination, oxide layers, etc.) play a role because the hydrogen must recombine at the surface before desorbing, and the desorption energy and recombination rate will depend on the surface. The history and treatment of the steel can greatly affect surface roughness and conditions. The quality of the sensors used in the outgassing measurements is also a concern. Measurement methods vary, but all depend on the absolute reading of some vacuum sensor, and often its linearity as well, yet the absolute calibration of vacuum sensors (i.e., the traceability to the International System of Units, or the SI) is often neglected in outgassing measurements. Practical vacuum chambers come in a variety of sizes and shapes and the stainless steel thickness will vary greatly between the chamber walls and flanges.

We are developing vacuum standards that operate in the UHV and XHV, an application that requires ultralow outgassing rates in an apparatus constructed from both custom and off-the-shelf stainless steel vacuum components. We sought the simplest techniques to produce the ultralow outgassing rates. In the present work, we tested nominally identical vacuum chambers subjected to different heat treatments. The vacuum chambers we tested were constructed of vacuum components of standard size and flange type, readily available from a plethora of commercial vendors. We chose to test medium heat treatment vacuum and air-bakes because these did not require a high-temperature vacuum furnace and can be performed in most laboratories. We constructed an apparatus that allowed outgassing rates of two nominally identical chambers with different heat treatments to be measured and compared under nominally identical conditions. Our objective was to achieve outgassing fluxes of 10^{-11} Pa $l\ s^{-1}\ cm^{-2}$ or better, which is an outgassing flux typically required for XHV. We posited that, if an air-bake could achieve this low outgassing flux, it would greatly simplify preparation of vacuum components. In fact, we found that the medium heat treatment in vacuum produced a better outgassing flux than the air-bake alone, and that the air-bake set-up was, perhaps, not simpler than the vacuum-bake. Another interesting result of the present work is that an air-bake

applied after a medium heat treatment vacuum-bake lowered outgassing flux by an additional factor of two.

II. EXPERIMENT

A. Sample preparation

Our samples are four identical SAE 304L (UNS S30403) stainless steel chambers, as shown in Fig. 1. The chambers are assembled from standard vacuum components: a standard tee, a standard nipple, and two blank flanges, all with DN40CF flanges, and a zero-length reducer flange (DN16CF to DN40CF). Not shown in Fig. 1 is the all-metal right-angle valve used to connect the chamber to the vacuum system via the DN16CF side of the zero length reducer. Two right-angle valves are part of the apparatus and common to all the samples. The chambers have an inner surface area of $348\ cm^2$ and a volume of $0.291\ l$, which includes the small volume and area of the valve up to the valve seat. The area was geometrically determined using the measured dimensions with an uncertainty of 0.1% ($k=2$). The chambers were cleaned using the following procedure: washing with a commercial detergent solution (sodium carbonate, 10%–25%; sodium dodecylbenzenesulfonate, 1%–10%; nonionic detergent, 1%–10%) using warm water and ultrasonic bath, rinsing with deionized water, immersing in ultrasonic bath with deionized water, rinsing with isopropyl alcohol, and blowing dry with nitrogen gas.

The four chambers were assembled as shown in Fig. 1. Oxygen-free high purity copper gaskets were used for the seals. These had negligible contribution to the outgassing because they are known to have outgassing fluxes on the order of 10^{-12} Pa $l\ s^{-1}\ cm^{-2}$ and comprised approximately 5% of the total chamber area.²¹ The chambers were designated as VAC1, LAIR2, DAIR3, and DAIR4, depending on their heat treatment. Chamber VAC1 was initially subjected to a medium heat treatment (under vacuum), chamber LAIR2 was subjected to an air-bake performed in the laboratory atmosphere, and chambers DAIR3 and DAIR4 were air-baked using clean dry volatile-organic-compound (VOC) free

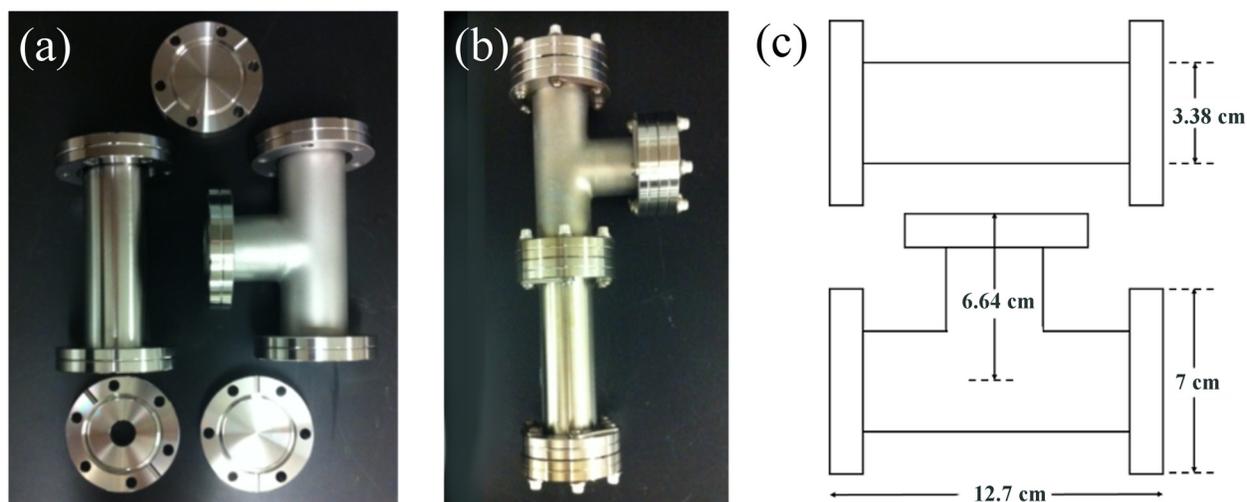


FIG. 1. (Color online) Standard vacuum components (a) used to construct four identical vacuum chambers (b). The nominal dimensions are shown in (c).

air. Chambers VAC1 and LAIR2 were initially prepared together: Chamber VAC1 was connected to an ultrahigh vacuum system and evacuated; chamber LAIR2 was placed next to the chamber VAC1 but was not evacuated and left exposed to the laboratory atmosphere. Both chambers were baked at 430 °C for 15 days by surrounding both with a cylindrical oven. During the bake, chamber VAC1 was exposed to vacuum on the inside surface and to ambient air on the outside, whereas chamber LAIR2 was exposed to ambient laboratory air on both sides. After the bake, VAC1 was cooled and vented to air. The outgassing rates of both of these were measured before baking and after baking. Chamber VAC1 was then subjected to an air-bake using dry-air (explained below), for 24 h at 430 °C.

Chambers DAIR3 and DAIR4 were subjected to dry-air bakes only, for 48 h at 430 and 250 °C, respectively. Both chambers were exposed to dry air on one side and to ambient air on the other side during bake. Dry VOC-free air was continuously flowed into the two chambers during the bake, and continuously pumped by a rough pump throttled by a valve, thereby maintaining atmospheric pressure in the two chambers during the bake.

B. Measurement apparatus and method

The schematic of the experimental setup is shown in Fig. 2. Two sample chambers (designated V_1 and V_2) of volume V_1 and V_2 were connected to the apparatus measurement chamber V_0 of volume V_0 , through valves X1 and X2,

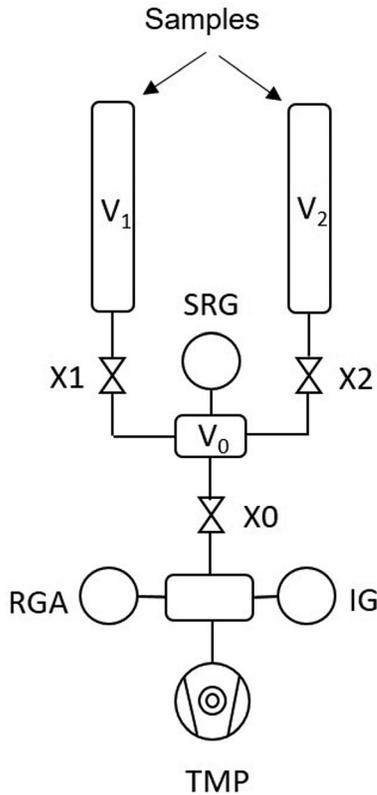


FIG. 2. Schematic of the apparatus used to determine the outgassing rates and fluxes of the sample chambers. Two identical sample chambers of volumes V_1 and V_2 can be mounted to the apparatus at the same time.

respectively. The volumes V_1 , V_2 , and V_0 were determined using an expansion method and are discussed in Sec. II C. A spinning rotor gauge (SRG) attached to the measurement chamber was used to determine the outgassing rates by the rate-of-rise method. An isolation valve X0 was used to separate the measurement chamber from a turbo-molecular pump, an ionization gauge (IG) and a residual gas analyzer (RGA). The apparatus was of all-metal construction, including the valves; all seals were of a knife-edge variety with copper gaskets.

A rate-of rise method was used to determine the outgassing rates of the sample chambers and measurement chamber. The outgassing of the sample chamber was characterized by first baking the system under vacuum at a temperature of 150 °C for 72 h to remove water absorbed on the surfaces of the system walls. Bakes at 150 °C are sufficient to remove most of the water absorbed on stainless steel surfaces, but are not high enough to remove a relevant amount of hydrogen dissolved in the bulk of the stainless steel, as will be evident from the proceeding discussion in Sec. III and Eq. (7). During this time, all valves were open. The system was continuously pumped by the turbomolecular pump to reach a pressure $p < 1 \times 10^{-7}$ Pa measured with the IG. Outgassing measurements were performed after this condition was reached. The outgassing of the measurement chamber represents a background signal that must be subtracted. This was measured by isolating the measurement chamber V_0 , closing the valves X1, X2, and X0, and observing the pressure rate-of-rise on the SRG. The SRG pressure measurement was absolute and SI traceable through a NIST calibration of the accommodation coefficient.²² The outgassing rate q_0 of the measurement chamber was determined from

$$q_0(T) = Q_0(T)A_0 = V_0 \frac{dp_0(T)}{dt}. \quad (1)$$

$Q_0(T)$ is the outgassing flux from the measurement chamber of the volume V_0 with area A_0 at a temperature T .

After the determination of the background outgassing flux $Q_0(T)$, the entire system was again evacuated to a pressure $p < 1 \times 10^{-7}$ Pa. Next, the outgassing rate of the combined chambers of volume $V_1 + V_0$ was measured using the rate-of-rise method with the valve X0 and X2 closed. The combined outgassing rate $q_{01}(T)$ is given by

$$q_{01}(T) = Q_0(T)A_0 + Q_1(T)A_1 = (V_0 + V_1) \frac{dp_{01}(T)}{dt}. \quad (2)$$

Combining Eqs. (1) and (2) leads to the expression for outgassing flux of the sample chamber

$$Q_1(T) = \frac{1}{A_1} \left((V_0 + V_1) \frac{dp_{01}(T)}{dt} - q_0(T) \right). \quad (3)$$

Thus the measured outgassing flux $Q_1(T)$ depends on the volumes V_0 and V_1 , the measured rate of rise, and the area of the sample chamber A_1 . The Type B uncertainty of the outgassing flux is estimated to be 10% ($k=2$) with a repeatability of 2% at the time of measurement.

The total relative uncertainty of the outgassing flux, as given by Eq. (3) is

$$u_{Q_1} = \sqrt{u_B^2 + u_A^2} \\ = \sqrt{u_{A_1}^2 + u_{V_0}^2 + u_{V_1}^2 + u_{p_{01}}^2 + u_{q_0}^2 + u_A^2}. \quad (4)$$

The type A uncertainty u_A is derived by statistical methods and is dominated by the reproducibility, as discussed below. The type B uncertainty u_B is derived using other methods and, unless stated otherwise, are given below as $k=2$ (95% confidence interval), as defined in Taylor and Kuyatt.²³ The volume uncertainties u_{V_0} and u_{V_1} are discussed in Sec. II C. The pressure rate-of-rise $u_{p_{01}}$ contributes the largest type B uncertainty component and is approximately 7%. It appears in both the $q_{01}(T)$ and $q_0(T)$ components of Eq. (3) and consists of the combined uncertainty of the effective accommodation coefficient (inverse calibration factor) determined for N_2 (<0.5%),²¹ the relative change in the effective accommodation coefficient for H_2 (6%),²⁴ the long-term stability of the calibrated effective accommodation coefficient (2%)²⁵ the estimated change due to heating the SRG to 150 °C (2%),²⁶ and the statistical uncertainty due the linear fit to the pressure rise data (2%). The uncertainty of the background outgassing rate $q_0(T)$ is approximately $u_{q_0} = 7\%$. The repeatability was determined without evacuating or rebaking the system between measurements. However, the reproducibility, determined from repeat measurements where the system was vented and rebaked between determinations, was approximately 20% and is much larger than the type B uncertainty. This large variation is likely due to real changes in the outgassing rate caused by changes in the surface of the stainless steel chambers when exposed to laboratory atmosphere and rebaked at 150 °C. Thus the total combined uncertainty of our measurements is approximately 20% ($k=2$). This uncertainty applies to all outgassing determinations reported here because all chamber outgassing rates were determined the same way.

C. Determination of the volumes

The volumes V_0 , V_1 , and V_2 were determined using a volume expansion method. First, a known volume V_C was attached to the measurement chamber. The known volume

TABLE I. Measured volumes of the apparatus and sample chamber. All four sample chambers used in this study had the same volume, V_1 .

Chamber	Volume (l)
V_C	0.118
V_0	0.091
V_1, V_2	0.291

consisted of a standard nipple of known dimensions. The combined volume $V_0 + V_C$ was filled with gas with the valve X1 closed and V_1 evacuated. The valve X1 was then opened and gas was allowed to expand into V_1 , thus lowering the gas pressure. The measured ratio of initial to final pressures was thus $R_C = (V_0 + V_1 + V_C)/(V_0 + V_C)$. The standard volume was then removed and the expansion procedure repeated. In the latter case the measured pressure ratio was $R_0 = (V_0 + V_1)/V_0$. Thus the volumes V_0 and V_1 were determined from the measured pressure ratios

$$V_0 = \frac{R_C - 1}{R_0 - R_C} V_C, \quad (5)$$

$$V_1 = \frac{(R_C - 1)(1 - R_0)}{R_0 - R_C} V_C. \quad (6)$$

The results of the expansion are given in Table I. We estimate that the determined volume uncertainty is 2% ($k=2$). All four of the sample chambers had volumes equivalent to V_1 to within the above stated uncertainty.

III. RESULTS AND DISCUSSION

The essential results of this study are summarized in Table II. We analyzed the data assuming all of the outgassing species was H_2 . After a single outgassing measurement, the collected gas was dumped to the RGA (Fig. 3); the majority of the gas (>95%) desorbed from the chambers was observed to be H_2 . We also report the “nitrogen equivalent” outgassing flux to facilitate comparison with authors who report outgassing results in nitrogen equivalent. The nitrogen equivalent rate is obtained by assuming the outgassing species is N_2 and using the N_2 sensitivity factor for the gauge sensitivity in the analysis of the outgassing data. A difference between the nitrogen equivalent rate and that for a specific species (e.g., H_2) only occurs for gauges sensitive to gas

TABLE II. Outgassing fluxes of the four sample chambers. Prior to the outgassing measurements, all sample chambers were exposed to laboratory air, evacuated, and baked at 150 °C for 72 h. Outgassing fluxes were measured for chamber temperatures between 20 and 21 °C.

Sample chamber	Heat treatment	Treatment temperature (°C)	Treatment time (h)	H_2 outgassing flux (Pa l s ⁻¹ cm ⁻²)	N_2 equivalent outgassing flux (Pa l s ⁻¹ cm ⁻²)	Fourier number F_0
VAC1	Before heat treatment	—	—	1.8×10^{-9}	4.7×10^{-10}	—
LAIR2	Before heat treatment	—	—	1.8×10^{-9}	4.8×10^{-10}	—
VAC1	Vacuum bake	430	360	1.9×10^{-11}	5.1×10^{-12}	3.24
LAIR2	Lab air bake	430	360	1.3×10^{-10}	3.4×10^{-11}	3.24
DAIR3	Dry air bake	415	48	3.8×10^{-10}	1.0×10^{-11}	0.36
DAIR4	Dry air bake	250	48	7.8×10^{-10}	2.1×10^{-10}	0.02
VAC1	Dry air bake	430	24	1.1×10^{-11}	3.0×10^{-12}	3.46 ^a

^aThis Fourier number combines the first bake (430 °C for 360 h) with the second in dry air (430 °C for 24 h).

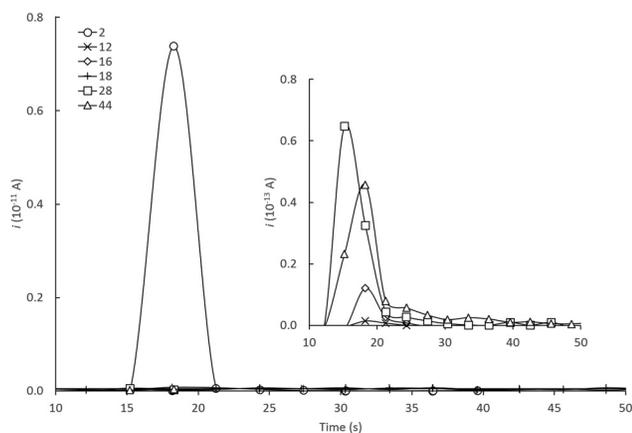


FIG. 3. RGA signal i for individual molecular masses as a function of time due to the release of the outgassing products. The gas-burst peaks are not fully resolved by the RGA; nevertheless, the traces demonstrate that mass 2 (H_2) is the dominant outgassing product.

species, such as the SRG. The relative difference between nitrogen equivalent rates can be only be compared if the same type of gauge was used for each determination.

The time it takes to reduce the hydrogen concentration in the stainless steel bulk depends on both the thickness of the material, d , and the bake temperature T . A dimensionless time, given by the Fourier number describes the relative reduction in hydrogen concentration²⁷

$$F_0 = \frac{4D(T)t}{d^2}, \quad (7)$$

t is the bake time at a temperature T . This enables a comparison to other works and the ability to extrapolate the present results to chambers of different thickness, bake times, etc. The diffusion constant has a strong dependence on temperature: $D(T) = D_0 \exp(-E_D/k_B T)$. We use the values of $D_0 = 0.0122 \text{ cm}^2/\text{s}$ and the activation energy $E_D = 0.57 \text{ eV}$ from Grant *et al.*¹⁶ to calculate the Fourier number. The Fourier number is very sensitive to E_D , and it is worth noting that choosing $E_D = 0.65 \text{ eV}$ from Mamun *et al.*,¹² for example, decreases the Fourier numbers in Table II by more than a factor of two. We use the flange thickness for d . The chamber thickness varies, but the geometry of all four chambers are identical, so the choice of d is somewhat arbitrary in the context of comparing the outgassing results among the heat treatment methods. The 72 h 150 °C bake to remove water is included in the Fourier numbers in the table, but only contributes $F_0 = 0.01$ to the Fourier number.

For chambers VAC1 and LAIR2, we measured outgassing before and after performing the medium temperature heat treatments. The initial outgassing rate was measured following the routine 72 h 150 °C bake, which was performed on all chamber samples to remove H_2O absorbed on the chamber surface prior to the outgassing measurements. The in-vacuum heat treatment improved the outgassing flux of chamber VAC1 by nearly 2 orders of magnitude whereas the air-bake only improved the outgassing flux of chamber LAIR2 by about 1 order of magnitude. Clearly the medium-heat treatment in vacuum is a better method.

The outgassing flux we achieved using the medium heat treatment method are similar to the outgassing flux of $2.4 \times 10^{-11} \text{ Pa s}^{-1} \text{ cm}^{-2}$ measured by Mamun *et al.* for a 400 °C bake at 100 h. We estimate their Fourier number to be 0.06. Our longer bake time and thinner flanges did not produce a significantly better outgassing flux, suggesting that the reduction in the outgassing is not solely determined by a simple diffusion model. Hydrogen atoms must recombine to desorb from the surface, and for large values of F_0 , the outgassing reduction may be limited by recombination and the presence of hydrogen traps.^{16,28} The outgassing flux for our medium temperature bake is also about 1 order of magnitude larger than that achieved by Park *et al.* for a similar heat treatment. Their values are close to that obtained by vacuum firing at 950 °C.⁸

One possible explanation is that the air-bake produced an oxide layer with a lower diffusion coefficient for H_2 than stainless steel. This would then form a “diffusion barrier” coating. It is then possible that the oxide layer formed early in the air-bake and prevented much of the hydrogen from diffusing out of the stainless steel. The high hydrogen concentration behind the oxide layer would slowly diffuse through the oxide layer, producing an outgassing rate that is better than an untreated chamber, but not as good as the chamber that was baked in vacuum and had a much lower concentration of hydrogen. To test this hypothesis, we performed an air-bake at a lower temperature that would form an oxide layer but degas little of the hydrogen. We also performed an air bake at a shorter time. Finally, we performed an air bake on the vacuum baked sample to see if the outgassing rate further improved.

We also switched from using laboratory air to dry VOC-free air. In some of our early tests, we had some difficulty with contamination occurring during air-bakes. This was mainly due to organic compounds degassing from heaters and insulating materials used during the bake, and becoming deposited on the steel surface. Flowing VOC-free air into the chamber during the bake was done to prevent this from occurring. In addition, the laboratory humidity varied and the humidity local to the chamber during the bake was not well controlled in our initial tests. Using clean dry VOC-free air removed this as a variable.

As seen from the Fourier number, the DAIR4 was not baked long enough or hot enough to remove a significant amount of hydrogen. Nevertheless, the outgassing rate improved by a factor of two over that of untreated steel. This supports the diffusion barrier hypothesis as it is unlikely that the outgassing is dominated by recombination at the surface for the low Fourier number. DAIR3 was baked for the same amount of time as DAIR4, but at a much higher temperature, and the outgassing rate showed an improvement over DAIR4 by a factor of about two. This seems reasonable, the temperature of DAIR3 was hot enough to degas some of the hydrogen from the bulk. The higher temperature may have also increased the oxide layer thickness.¹⁸ Note that the diffusion coefficient used to determine the Fourier number was that of stainless steel, not of the oxide layer. If the oxide layer is presumed to have a smaller diffusion coefficient, then the Fourier numbers reported in Table II represent an upper limit.

We then took VAC1 and performed an air-bake with the clean dry VOC-free air. The outgassing flux dropped by another factor of 2. A Fourier number greater than 1 indicates that the outgassing is no longer in the diffusion-limited regime and the 24 h bake was not long enough to significantly reduce outgassing via diffusion through the stainless steel bulk. If the outgassing is recombination limited, it is likely that oxide layer modifies the surface in such a way as to reduce recombination and thus reduce the recombination-limited outgassing rate. Our result stands in contrast to those of Park *et al.*, who did not see a significant difference between air bakes and medium temperature vacuum bakes; in fact, their air bake outgassing rates were slightly lower than their vacuum bakes. Bernardini *et al.*²⁹ also conclude that most of the outgassing reduction in an air-bake is due to hydrogen diffusion from the bulk. The present results are not in contrast to this hypothesis, but do support the hypothesis that an oxide layer can improve outgassing rates by modifying the surface reaction rates.

IV. SUMMARY AND CONCLUSIONS

We have determined the outgassing fluxes of four identical chambers constructed of common 304L stainless steel vacuum components. Each was prepared using different heat treatments to reduce the hydrogen outgassing rate. Chamber VAC1 was baked under vacuum at 430 °C for 15 days, and chamber LAIR2 was baked in air at 430 °C for 15 days. The outgassing flux of VAC1 was an order of magnitude smaller than that of LAIR2. Chamber VAC1 was then baked in air for 24 h at 430 °C, resulting in dropping the outgassing flux by another factor of two. This strongly suggests that the oxide layer modifies the surface to reduce hydrogen desorption. We baked chamber DAIR4 in VOC-free dry air for 48 h at 250 °C, and DAIR3 for 24 h at 415 °C. The bake temperature of DAIR4 was too low and the time too short to provide significant outgassing of hydrogen from the bulk, but the outgassing flux nevertheless improved by a factor of two. Given the small Fourier number, it seems like the oxide layer acted as diffusion barrier. Chamber DAIR3 had another factor of two improvements over DAIR4, consistent with a thicker oxide layer.

The aim of this study was to obtain ultralow outgassing rates and fluxes using standard vacuum components and inexpensive, simple, laboratory techniques. Of the two methods investigated, medium-temperature vacuum versus air-bake, the medium-temperature vacuum bake produced the lowest outgassing flux. A subsequent air-bake lowered the outgassing flux even more. We also found the air bakes to be somewhat inconvenient because great care had to be taken to insure that the parts would not become contaminated during the bake. The medium-temperature vacuum bake was sufficient to obtain H₂ outgassing flux on the order of 10⁻¹¹ Pa l s⁻¹ cm⁻².

Our results are somewhat in contrast to those of Park *et al.* because they only saw a small difference between

air-bakes and medium-temperature vacuum bakes, with the air-bake being the lowest. This may also point to a concern with the air-bakes: oxide thickness may be important, which may depend on bake temperature, duration, initial surface conditions, and geometry. Pores or cracks in the oxide layer may also influence the outgassing rate. It is possible that these complications may explain the differences between our results and those of Park *et al.* We did not perform surface analysis on our samples and so we did not know our oxide thickness or structure. Such careful control over the oxide formation does not make for a simple technique.

¹UHV and XHV are defined in an AVS document to be $\leq 10^{-7}$ and $< 10^{-10}$ Pa, respectively [Dictionary of Terms for Vacuum Science and Technology, edited by M. S. Kaminsky and J. M. Lafferty (AIP, Woodbury, 1980)]. This contrasts with the German Institute of Standardization definition of UHV as $\leq 10^{-5}$ Pa (DIN 28400), but the DIN standard has no definition of XHV. We find that in present common usage, the scale of 10^{-10} Pa (e.g., 5×10^{-10} Pa) is often considered to be XHV. The AVS document was not produced by a standards organization, is nonbinding, and somewhat outdated. For these reasons, we elect to define XHV as $< 10^{-9}$ Pa.

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