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Reduction in hydrogen outgassing from stainless steels by a medium-temperature heat treatment

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The authors carried out heat treatments, in-vacuum or in-air at 400 °C, to reduce the hydrogen outgassing rate from stainless steels. An outgassing rate as low as 2×10^{-14} Torr s^{-1} cm^{-2} was routinely achieved by a medium-temperature bakeout, but it took much longer time than reported to perform intensive thermal treatment. The result shows that the diffusion process governs degassing only at the early stage of degassing while the recombination limits outgassing at low concentrations.

Air baked chambers had somewhat lower outgassing rates than in-vacuum baked chambers, suggesting that the surface oxide acts as a further barrier for H2 outgassing. However, the main effect may be attributed to the removal of mobile hydrogen through diffusion. The results showed that the ultralow outgassing rate can be reproducibly achieved for stainless steel chambers with the established heat treatment procedure. The study also showed that the ultralow outgassing property of a treated chamber can be restored by a low temperature (>150 °C) postbakeout, after exposure to ambient air. © 2008 American Vacuum Society. [DOI: 10.1116/1.2956625]

I. INTRODUCTION

Stainless steel (SST) is the most common construction material for ultrahigh vacuum (UHV) chambers because of its good vacuum and mechanical properties. Since outgassing of hydrogen often limits the base pressure of a SST vacuum system, many efforts have been made to reduce the hydrogen outgassing rate by using thermal treatments. Very low outgassing rates, less than 1×10^{-13} Torr s^{-1} cm^{-2}, have been achieved with the treatments.1

However, further reduction in the SST hydrogen outgassing rate is still desired: (1) to reduce the pumping requirement and (2) to convert UHV to extreme high vacuum (XHV). Reducing the pumping requirement is one of the key issues for a large, conductance-limited vacuum system, as in particle accelerators whereas conversion of UHV to XHV is a prerequisite of the dynamical surface studies.2 XHV is also essential for some applications of a new generation accelerator, for example, to increase the lifetime of the photocathode electron source of the Cornell Energy Recovery Linac (ERL), being built at Cornell University.3

Advances in practical methods of reducing the outgassing rates make it possible to obtain extremely low outgassing rates.4,5 Although many efforts have been made to reduce the outgassing rate for hydrogen, recent improvements are tending toward reducing the time and temperature required to obtain a low outgassing rate.4 Two good examples are the air bakeout at 400°C rather than vacuum firing at 950°C and the construction of a very thin insulating panel instead of a thicker vessel with integrated getters.4,5 Thus the extremely low outgassing rates can be achieved more efficiently and economically. In such methods, it is generally accepted that hydrogen diffusion plays an important role in degassing during the heat treatment. Therefore, it is preferred to build a vacuum chamber as thin as possible and to bake the chamber at a higher temperature.

The aim of this study is to establish a thermal treatment procedure that can reproducibly yield an extremely low outgassing rate in SST. The thermal treatment established by us is then applied to the construction of the ERL vacuum system or even to existing vacuum systems. We adopted a medium-temperature bakeout to obtain an extremely low hydrogen outgassing rate, lower than 10^{-13} Torr s^{-1} cm^{-2}, which was rather easily applied to the construction of a low outgassing SST chamber. The processing temperature time was preset to 400 °C for ~96 h, because the diffusion theory predicts that outgassing can be lowered by a factor of more than 1000. Furthermore, to take advantage of the thin vacuum chambers, we selected a relatively thin material (thickness=1.65 mm) after considering the structural integrity. Two commonly used materials of SST types 304L and 316L were tested and compared.

II. EXPERIMENT

SST samples were made in the form of a cylindrical chamber, cut from the same mill run. All chambers were identical in length (150 cm) with a 15 cm inner diameter. The wall thickness (d) is 1.65 mm except sample 5. We made efforts to make the thickness of all parts the same as the chamber wall. The circular SST plates (d=1.65 mm) were directly welded on both ends of the cylinder, then two small ConFlat flanges (DN40) were attached on both end plates. The total inner surface area is about 7600 cm² and the volume is 28 l. All the tubes and the end plates were degreased using detergents, rinsed with de-ionized water, welded, and helium leak checked prior to the tests.

Footnote:

4 Electronic mail: yf67@cornell.edu
The main method used to measure the outgassing rate is the so-called rate-of-rise (RoR) method.\(^8\) This method is suitable when the pressure increases linearly with time over a long period, which is generally the case for hydrogen outgassing from the SST vacuum chamber after a heat treatment. If the outgassing rate is constant over a long period, the adsorption may be zero. Thus we can measure the intrinsic hydrogen outgassing rate \(q\). The \(q\) is calculated using \(q = (V/A)(dP/dt)\) Torr \(\ell\) \(s^{-1}\) \(cm^{-2}\), where \(V\) is the volume of the test chamber, \(A\) is the geometrical surface area of the sample chamber, and \(dP/dt\) is the measured rate of pressure rise on a sealed-off sample chamber at a constant room temperature with no pumping. All values in this study are hydrogen equivalent because, as measured by a residual gas analyzer, the dominant residual gas was \(H_2\) after the bakeout.

The experimental setup is shown in Fig. 1(a). An oven was used to perform the heat treatment up to 400 °C and also to carry out the pressure rise measurement. Additional vacuum instruments were placed outside the oven due to their temperature limitation. All the outgassing rate measurements were carried out with the following procedures.

1. A stainless steel sample chamber was subjected to a heat treatment at 400 °C in the bakeout oven for a prescribed duration.
2. The heat-treated chamber was exposed to ambient air for a period of at least 8 h.
3. The chamber was connected to the system as shown in Fig. 1(a), evacuated with a turbomolecular pump and helium leak checked.
4. The chamber was baked in the oven to various temperatures between 150 and 250 °C for \(\sim 100\) h, and the setup outside of the oven was always baked out at 250 °C.
5. The entire system was leak checked again after cooling down from the post-treatment bake.
6. Outgassing rate measurements of the postbaked chamber were then carried out at ambient temperature using RoR method and/or throughput method.
7. Steps 2–6 were repeated to measure the dependence of the outgassing rate on the post-treatment bake temperatures.

For the RoR measurement, a spinning rotor gauge (SRG) was used to prevent significant errors caused by either pumping or outgassing action of an ion gauge. Proper operation of the SRG is very important in ensuring the precise measurements of extremely low outgassing rates. The temperature control is especially important. An active temperature control system, consisting of a cooling coil at constant temperature of 15 °C and a proportional-integral-derivative controlled heater, was deployed in the oven, and the temperature was stabilized to 25 ± 0.1 °C during a RoR measurement. With this temperature stability, one day was enough for the measurement of a RoR as low as \(1 \times 10^{-7}\) Torr/\(\ell\) day irrespective of the noise. A typical set of RoR data is given in Fig. 1(b), showing a linear rise of pressure in time.

The SST outgassing rates obtained by RoR were also cross-checked by the throughput (TP) method that uses a small orifice (with a \(H_2\) gas conductance of 0.52 \(\ell\) \(s^{-1}\)), as shown in Fig. 1(a). The steady-state outgassing rate is calculated by the measured pressure difference, \(\Delta P\), across the thin orifice, \(q = (C_{\text{orifice}}\Delta P)/A\) (Torr \(\ell\) \(s^{-1}\) \(cm^{-2}\)). A TP measurement was always performed immediately after a round of RoR measurement. Though the uncertainty of the TP measurements were normally not as good as the RoR method because of very small pressure difference across the orifice, the TP methods generally yielded outgassing rates that were similar to those measured by the RoR method. It is important to point out that the TP method and the RoR method are performed at very different pressure scales. In the TP method, the outgassing rates are measured at pressures in the low \(10^{-10}\) Torr range owing to the extremely low outgassing rate. On the other hand, in the RoR method, the outgassing rates are measured at the pressure in the high \(10^{-7}\) Torr to the low \(10^{-5}\) Torr range where the SRG is effective. The agreement between the two methods is a clear indication of independence of the outgassing rate on the system pressure.

III. RESULTS AND DISCUSSION

A. Reduction in outgassing using a medium-temperature bakeout

Prior to the heat treatments, the unprocessed hydrogen outgassing rate \(q\) for 304L (sample 1) was measured after...
Table I. Comparison of H₂ outgassing rates between types 304L and 306L SSTs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample No.</th>
<th>In-vacuum heat treatment</th>
<th>Fo</th>
<th>Postbakeout</th>
<th>ΣFo</th>
<th>q (Torr  ( \ell ) s⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>1</td>
<td>200 °C, 96 h</td>
<td>0.13</td>
<td>2.7 \times 10⁻¹²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 °C, 96 h</td>
<td>12.8</td>
<td></td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 °C, 100 h</td>
<td>14.0</td>
<td></td>
<td>14.1</td>
<td>1.8 \times 10⁻¹⁴</td>
<td></td>
</tr>
<tr>
<td>306L</td>
<td>3</td>
<td>200 °C, 96 h</td>
<td>0.13</td>
<td>6.3 \times 10⁻¹²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 °C, 96 h</td>
<td>10.3</td>
<td></td>
<td>10.3</td>
<td>4.3 \times 10⁻¹⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 °C, 96 h</td>
<td>10.3</td>
<td></td>
<td>10.4</td>
<td>1.2 \times 10⁻¹⁴</td>
<td></td>
</tr>
</tbody>
</table>

As pointed out by several authors, after intensive heat treatment (Fo > 3), atomic hydrogen recombination on the SST surface may become a rate limiting step in H₂ desorption. This may explain the slowing down of the outgassing rate reduction as shown in Fig. 2. Thus a much faster reduction, the q decreases with a slower slope, suggesting that the outgassing may be governed by some mechanism other than bulk diffusion.
may be attributed to the surface effects, as the surface of stainless steel is known to be modified after 250–450 °C vacuum annealing and successive air exposure. The results in Tables I and II clearly show that reduction in $q$ was indeed reproducible. Thus it is reasonable to conclude that the outgassing rate for both 304L and 316L can be lowered to $2 \times 10^{-14}$ Torr s$^{-1}$ cm$^{-2}$ with sufficient heat treatment in air or in vacuum.

B. In-vacuum versus in-air heat treatment at 400 °C

It is generally believed that the bakeout of stainless steels causes symmetrical H$_2$ outgassing from both surfaces in a space that contains sufficiently low H$_2$ contents. If the diffusion model holds for the degassing process, the bakeout may produce a similar outgassing rate regardless of the environments whether in vacuum or in air.

We compared such effects on the reduction in outgassing rates to see if there are any differences or additional benefit of the in-air heat treatment over the in-vacuum heat treatment. The heat treatments were done for $F_o \geq 10$, either in air or in vacuum.

C. Outgassing rates versus postbakeout temperature

It is certain that an in-vacuum bakeout is needed to achieve the UHV or XHV level required for a vacuum system constructed from the heat-treated stainless steel materials due to air exposure during assembly and installation processes. Therefore, the postbakeout temperature is one of the key practical parameters. We measured the effect of postbakeout temperature on the outgassing rates of heat-treated SST sample chambers. The postbakeout temperatures were limited to a range of 150–250 °C that are typical in situ procedures to remove the water molecules adsorbed on the surface during air exposure. Before each measurement, the test chamber was exposed to ambient air instead of nitrogen for >8 h to simulate the process close to practical situations. The results are shown in Fig. 3(a) for SST 304L and Fig. 3(b) for SST 316L, indicating no clear dependence of the

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample No.</th>
<th>Pretreatment</th>
<th>Fo</th>
<th>Postbakeout</th>
<th>$\Sigma F_o$</th>
<th>RoR</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>1</td>
<td>400 °C/96 h, in vacuum</td>
<td>12.8</td>
<td>150 °C, 72 h</td>
<td>13.0</td>
<td>$1.9 \times 10^{-14}$</td>
<td>⋯</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>400 °C/100 h, in vacuum</td>
<td>14.0</td>
<td>200 °C, 80 h</td>
<td>14.1</td>
<td>$1.8 \times 10^{-14}$</td>
<td>$2.5 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>400 °C/96 h, in air</td>
<td>13.6</td>
<td>150 °C, 96 h</td>
<td>13.7</td>
<td>$1.2 \times 10^{-14}$</td>
<td>⋯</td>
</tr>
<tr>
<td>316L</td>
<td>6</td>
<td>400 °C/77 h, in vacuum</td>
<td>10.3</td>
<td>150 °C, 96 h</td>
<td>10.4</td>
<td>$1.2 \times 10^{-14}$</td>
<td>$3.0 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>400 °C/77 h, in air</td>
<td>10.3</td>
<td>150 °C, 96 h</td>
<td>10.4</td>
<td>$8.5 \times 10^{-15}$</td>
<td>⋯</td>
</tr>
</tbody>
</table>

Fig. 3. Dependence of $q$ on the postbakeout temperature: (a) for SST 304L and (b) for SST 316L. Data were taken at 25 °C. The orders of measurements were 150, 200, and 250 °C. After each measurement, the chamber was exposed to ambient air for >8 h.
outgassing rate on the postbakeout temperature in this temperature range. Therefore, only a mild bakeout, with temperature and duration sufficient to remove the water on the surface, is necessary to restore the extremely low H₂ outgassing rate for the heat-treated SST system after exposure to ambient air.

As mentioned earlier, our results indicate that the surface atomic hydrogen recombination may govern the hydrogen outgassing after the intensive heat treatment, Fo ≥ 10. The diffusion theory predicts that, even after the intensive bakeout, a higher temperature bakeout would always yield a lower outgassing rate, and that the rate should be increasingly lower with repeated bakeout. This is certainly not what we have observed. Contrary to the prediction of the diffusion theory, the recombination of hydrogen at the surface may limit the outgassing phenomena when the hydrogen concentration of the bulk is sufficiently lowered. Since the recombination process is a much slower process, the outgassing rates seem to have remained almost the same.

D. Outgassing rates with thick SST material

On the other hand, we observed a different behavior when we intentionally added thicker walls to the test chamber. Two thick disks (d=20 mm) were directly welded on both side ends of the tube (d=1.65 mm) to simulate a practical situation of thick blank flanges. The chamber (304L) was heat treated for 96 h at 400 °C in air. After the evacuation followed by a 150 °C/96 h postbakeout, an outgassing rate of 6.4×10⁻¹⁴ Torr ℓ s⁻¹ cm⁻² was measured. However, unlike what was observed from the thin wall SST chambers, the value of q increased with higher postbakeout temperature (Fig. 4).

Two observations may be drawn from the results shown in Fig. 4. First, with similar heat treatment, the measured q was found to be more than a factor of 5 higher for the thicker chamber than that for the chambers with only thin walls (d=1.65 mm). This is not a surprise when the Fo number is taken into consideration. For the thicker parts of the chamber (d=20 mm), the prescribed heat treatment (that is, 96 h at 400 °C) only yields a Fo value of 0.08. If we assume the outgassing rate of the thinner part of the chamber to be the same as the value of sample 4, i.e., q=1.2×10⁻¹⁴ Torr ℓ s⁻¹ cm⁻² (air baked, Fo~14), the q from the thick walls can be estimated from the simple relation: \( Q_T = Q_{\text{thin}} + Q_{\text{thick}} \), where \( Q_T \) is the total measured outgassing rate, \( Q_{\text{thin}} \) and \( Q_{\text{thick}} \) are the outgassing from the thin walls and the thick walls, respectively. Then the estimated outgassing rate for the thick parts is 1.5×10⁻¹² Torr ℓ s⁻¹ cm⁻². This indicates that the heat treatment was rarely done for the thicker material, thus the diffusion process mainly governs the outgassing mechanism for the thick walls.

Second, higher q was resulted with higher postbakeout temperature. This phenomenon may be interpreted by the diffusion model. With a heat treatment of Fo=0.08 for the thicker walls, spatial distribution of hydrogen is sinusoidal with a higher concentration in the bulk. During a postbakeout at higher temperature, the bulk hydrogen outward diffusion outpaces the molecular hydrogen desorption via surface recombination. This leaves a higher hydrogen concentration near the surface when the chamber is cooled down, thus results in a higher outgassing rate at room temperature. Therefore, a higher temperature bakeout exhibits a higher outgassing rate. The fact may be true with an underdegassed vacuum chamber.

IV. SUMMARY

A medium-temperature bakeout was applied to reduce the hydrogen outgassing rate from stainless steel types 304L and 316L. The heat treatments were performed in vacuum or in air at 400 °C. The results may be summarized as follows.

1. Based on the hydrogen diffusion model, the level of heat treatment of stainless steels can be gauged by a dimensionless time, Fo, that is related to the hydrogen diffusion in the stainless steels. Ultralow outgassing rate of 10⁻¹⁴ Torr ℓ s⁻¹ cm⁻² range can be reproducibly obtained in stainless steels (both types 304L and 316L) with Fo ≥ 10 (for example, 77 h at 400 °C for d=1.65 mm).

2. Bulk hydrogen diffusion process governs the initial removal of hydrogen from SST, while hydrogen surface recombination plays an important role in degassing at lower hydrogen concentration.

3. Air baked samples had slightly lower outgassing rates than in situ baked ones for both 304L and 316L after the same heat treatment, suggesting that the oxide acts as a further barrier for H₂ outgassing at the surface. However, the main effect is more likely to be merely the removal of mobile hydrogen.

4. After intensive thermal treatments, the q showed no clear dependence of the outgassing rate on the postbakeout temperatures in the range of 150–250 °C, indicating that the recombination may be the prevail-
ing process for the outgassing. In other words, one can fully restore the ultralow outgassing rate in SST with a postbakeout temperature as low as 150 °C, after a heat-treated chamber is exposed to ambient air. Being able to achieve UHV and XHV with low temperature bakeout is extremely beneficial for applications such as particle accelerators.

In conclusion, we established a heat treatment procedure for stainless steel materials to reproducibly achieve ultralow outgassing rate. This procedure has been applied in the construction of the vacuum chambers and the in-vacuum components for a load-locked dc photocathode electron gun for the Cornell prototype energy recovery LINAC injector project.

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