

How Low Can You Go? Part 6 But a Few Settle for Treatment

Introduction

Back in the dark ages of 2003 I wrote a series of Lesker Tech[™] articles titled “How Low Can You Go?” Basically it examined ways of reducing a chamber’s gas load using heat, light, or a pick-axe to encourage contaminant atoms/molecules to release from the chamber’s surface into the gas phase during pumping.

In re-reading those old issues – it was a slow day – I realized that I didn’t really describe an olio of other methods for avoiding/reducing gas loads that have one common characteristic: they don’t readily fit in the heat, light, pick-axe categories. Oh, at some fundamental thermodynamics (sorry about the curse word) level there’s possibly a little heat/light going on. But at the level I’ll explain them, all these methods are about modifying the chamber’s surface, or what is stuck to it, with good old-fashioned chemistry. Yes, that’s right, we’re headed back to the *terra incognita* you abandoned in high-school.

- Removing surface contaminants prior to evacuation
- Making the surface less attractive to contaminants
- Chemically releasing surface contaminants into the gas phase
- Suppressing contaminant release from surfaces

Perhaps the best collective name for these techniques is *Surface Treatment*.

I make no claim this list is complete, nor do I give any DIY instructions. This is just a bunch of suggestions intended to fire up your imagination and get you search-

ing for gas load reduction methods that work for your system.

A final introductory note to new readers: if you’re not familiar with terms like *outgassing rate* or *gas load*, don’t start here. Go back through the Lesker Tech Archives and read the relevant issues.

Overview

The Surface Treatment methods can be loosely bundled into four groups:

1. Surface Modification
2. Surface Coating
3. Real Chemistry
4. Glow Discharge

Methods under groups 1 and 2 are typically a one-time deal applied before or during chamber construction. Methods under groups 3 and 4 are applied to fully assembled, thoroughly leak-checked, systems. Interestingly, if the process continuously contaminates the chamber, methods in groups 3 and 4 can be applied any time you need to whip the base pressure back into line.

Surface Modification

Mechanical Polishing

Commercially available stainless steel sheet, mechanically polished to a mirror finish, can be rolled and seam welded into cylindrical chambers. Some UHV experts frown on this approach, claiming the surface’s flashy appearance obscures the fact that the original inclusions and perhaps defects are just buried, not removed, by polishing. There

is also the issue of the mysterious Beilby layer: an amorphous metal surface layer covered with oxide, apparently produced by a high degree of mechanical buffing, that may act as a good depository for water and other contaminants.

Our experience making high vacuum chambers from mirror polished stainless sheet does not <pun alert> reflect those concerns. All other factors being equal, comparing a mirror-polished chamber with a cleaned brush-finished chamber one might reasonably expect at least a half-decade improvement in base pressure (in the same pump-down time). One difficulty in estimating that expectation is, polished cylindrical chamber walls are OK but what about the outgassing from the chamber’s end-plates, ports, and blank flanges? Those parts are rarely mirror-polished.

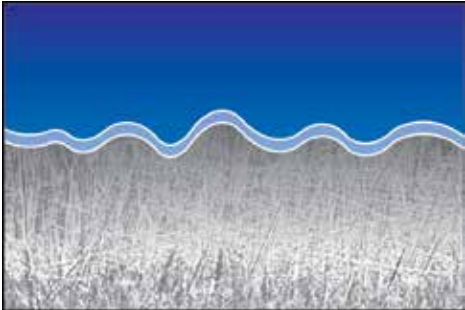
Electropolishing

Electropolishing, noted in passing in the original HLCYG series, is a chemical surface modification that is often very effective at reducing gas load. The chamber is made the anode of an electrolytic cell and filled with a mixed acid electrolyte. If you know anything about electroplating, look on this as the reverse process. The chemical details, although wonderfully exciting, aren’t exactly important but it’s worth knowing the process smooths the stainless by dissolving the surface’s micro-peaks more rapidly than its micro-dips.

Again, UHV experts aren’t encouraging about the process, suggesting electropolishing doesn’t do much to reduce the ‘real’



Surface Profile before Electropolishing



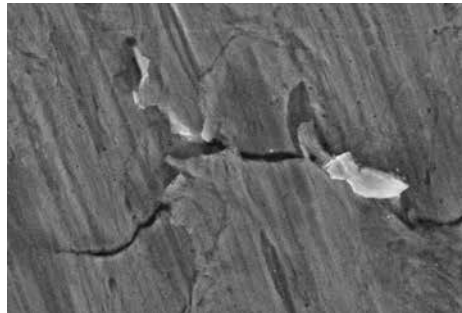
Surface Profile after Electropolishing

surface area. Some suggest the process may even add hydrogen to the near-surface layers of the bulk stainless and does nothing about non-conducting inclusions. However, it is acknowledged that the process passivates the surface with a thin, relatively ordered oxide layer that cures the Beilby blues and may even reduce the rate of hydrogen diffusion from the bulk stainless.

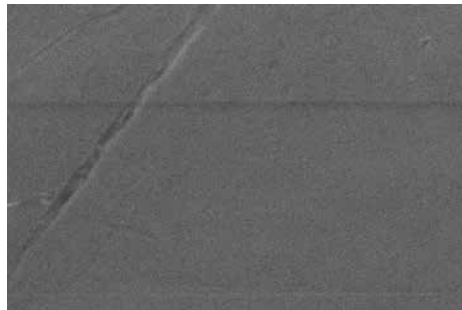
Our experience with electropolished chambers indicates a substantially improved base pressure compared to chambers with any other finish (all other things being equal), perhaps as much as a decade lower. In part that's because, if the electropolishing company is on top of its game, all interior surfaces are polished, not just the cylindrical bit as when using mechanically polished stainless.

Chemical Brightening

Alternative polishing methods for stainless and aluminum chambers include electro-less chemical etchants: the so-called brighteners or brightening processes. In the distant past I worked at a facility where vacuum chambers were treated with brightener solutions. I wasn't privy to the reasons or results but can only assume someone knew, or anti-



Original 'mill' finish (x5k)



Electropolished finish (x5k)

pated, that brightening had a positive effect, hopefully on the chambers' base pressure. An internet search turned up just a few links associating vacuum and brighteners but, since they were all lurking behind obscure pay-walls, I didn't look.

Surface Oxidation

Processes and results vary, but baking stainless surfaces in air between 150°C and 450°C to produce a thick, mostly chromium, oxide layer is regarded as an inexpensive and effective way of reducing subsequent gas load. Particularly noted is the reduction of hydrogen's diffusion rate from the bulk stainless as UHV pressures are approached.

One example in the literature states that a stainless surface oxidized at 250°C and subsequently baked under vacuum (unfortunately at an unstated temperature) had an outgassing rate of $\sim 3E-14$ Torr.liter/sec.cm² which is $\sim 7x$ lower than the outgassing rate published for stainless that has been vacuum fired at 900°C for 2 hours – not bad at all!

Surface Coating

Titanium Compounds

Work in the late 70s indicated stainless surfaces coated with TiN had an outgassing rate 1/5 that of uncoated stainless. Later work, comparing electropolished 304L stainless to the same material coated with 1 micron thick TiN layer, indicated a 100-fold reduction in hydrogen outgassing rate. However, more recent work suggests thick TiN layers, “. . . result in high water adsorption into the porous film and cause unwanted outgassing characteristics.” So the jury may still be out on this method's efficacy (or perhaps it's just my selection of reading materials).

Aluminum Oxide

About 20 years ago in a research lab I was visiting overseas I was shown a vacuum component that had been initially coated with aluminum (by a deposition method the staff were at pains to hide) which was then oxidized in a controlled, and again secret, way that limited grain boundary formation. The resulting surface looked . . . ethereal, almost not there. I was assured this surface's outgassing rate was substantially lower than an untreated surface since the coating had very low water vapor adsorption. While the coating had been used extensively in chambers and components around this lab, I don't believe the method was ever commercialized. Interesting idea though.

Silicon (Silicide?)

Using CVD processing initially developed in the mid-80s, SilcoTek™ has shown that silicon “. . . applied to and incorporated into . . .” a stainless steel component's surface can dramatically reduce outgassing. Quoting the website, “After 10 hours under vacuum at 61°C, the SilcoGuard™ 1000 coated part demonstrated a 14-fold lower outgassing rate than the heat-cleaned part.”

Real Chemistry

Nitric Oxide

Several advantages are noted for nitric oxide (NO) cleaning SS compared to the 'rival' technique of glow discharge: NO cleaning gives no ion sputtering or burial; no electrodes needed; no need for additional power supplies; no surface damage; and the technique is appropriate for a chamber of any shape containing any configuration of components. (Regrettably, I must admit I stole the 'no' jokes.)

In practice, flowing low pressure NO through a chamber oxidizes any adsorbed CO, hydrocarbons, and even carbonaceous material to give CO₂ and H₂O vapor (vapor because of the high wall temperature) which can be pumped away. Results in the literature, for incidental and deliberate hydrocarbon contamination, suggest clean-up is rapid, with RGA monitoring showing reductions in hydrocarbon peak amplitudes between 2 and 6 decades (depending on conditions and contamination levels). One potential disadvantage—for best results the chamber is heated (200°C) while the reactive gas is flowing.

Dichloropropane

An interesting 'chemical' idea is to flow a gas through the chamber that reacts with adsorbed water. A number of gases have been tried (including silanes and halogens) but dichloropropane is preferred by one research group. The time to reach 10⁻⁸ Torr using this cleaning technique shortened by factors between 4 and 500 compared to untreated surfaces. While 500x quicker is very impressive, I can't help wondering: the by-products are volatile oxygen-propane compounds and hydrogen chloride . . . HCl? In my pumps?

Glow Discharge

Applying appropriate (DC, RF, or DC/RF combination) voltages between an electrode and the chamber filled with a low pressure gas causes glow discharge to form (basically a plasma). For chamber cleaning we can ignore the plasma's complex details and just view it as a source of: ions (positive and possibly negative), electrons, radicals (chemical type, not political), and hot (excited) atoms that will flood to the chamber walls depending on local conditions/voltages.

How does a glow discharge clean a surface? In a variety of ways, some explained in earlier parts of the HLCYG series: (a) effectively 'heating' by electron or hot atom bombardment; (b) a little 'lighting' if the process gas's glow contains radiation in the deep UV; (c) ion sputtering, which might be equated with super-hot localized 'heating'; (d) but mostly by honest, old fashion chemistry, where the contaminants depending on their nature, are converted into H₂O, CH₄, or CO by ion, radical, or hot atom reactions and released into the gas phase where they are transported to the pumps.

Gas pressures range from 0.5 to 10 mTorr, although the initial 'strike' pressure for the glow may be 10x higher. Gas composition is chosen depending on the contaminants and the chemistry required to remove them. For example, oil or grease contamination may be addressed with O₂ or O₂ containing mixtures, even air. Hydrogen is used to convert 'carbonaceous' deposits to CH₄ and to help reduce metal oxide layer if it is an outgassing issue. Argon or helium are used where physically sputtering the surface will help, say, in getting water into the gas phase.

Glow discharge is particularly useful for cleaning stainless and aluminum cham-

bers with simple geometries—for example, spheres and tubes used in beam lines, accelerator tubes, and tokomaks that must reach UHV pressures with minimum outgassing due to photo-desorption. One report about cleaning multiple aluminum storage ring tubes noted that an argon glow discharge for three hours gave roughly the same outgassing rate reduction as baking at 200°C for 140 hrs.

For chambers with complex shapes or lots of metal bits sticking into the main volume, it may be less successful. But even then, the discharge equipment's low cost and process's low risk may make it worth trying.

Summary

Reducing outgassing rates by surface treatment can be assistive or an alternative to the traditional bake-out or more high-tech UV radiation methods. Although surface treatments mostly involve chemistry, truth is, you don't need to understand the reaction pathways to use the techniques. Just find a method that seems to best suit your equipment, application, pressure requirements, etc. and give it a whirl.