Low Outgassing of Silicon-Based Coatings on Stainless Steel Surfaces for Vacuum Applications

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ABSTRACT

Comparative tests of stainless steel vacuum chambers and components with and without silicon-based passivation coatings showed exceedingly low rates of gas evolution from the coated surfaces. A variety of approaches have been used to illustrate the low outgassing qualities of vacuum systems and vacuum components modified with an amorphous silicon (a-Si) deposition layer. For example, the samples are heated and cooled in turn while the outgassing rates are recorded at temperatures up to 250°C. Base pressures ranged from 10^{-7} Torr to 2.5 x 10^{-10} Torr. In other experimentation, the outgassing characteristics of systems in the 10^{-5} to 10^{-7} Torr vacuum range are compared. The coatings are resilient, inert and capable of withstanding temperatures above 400°C. As well as their obvious potential for reducing outgassing rates in vacuum chambers thereby allowing shorter pump-down times with smaller vacuum pump systems, they have proved useful in minimizing errors due to thermal desorption in experimental metal-envelope ionization gauges operating down to the low 10^{-10} Torr range.

INTRODUCTION

A vacuum leak notwithstanding, the presence of water, carbon monoxide, carbon dioxide, and hydrogen, as well as organic contamination on the walls of a vacuum system is the root cause for extended evacuation times. There are several techniques for the efficient removal of these contaminants. Appropriate surface cleaning and applied heat is certainly the first line of defense for organic contamination and water vapor removal [1-3]. Surface preparation through surface finishing and/or plasma treatments have also been applied to render the surfaces of a vacuum system free of contamination [1-3]. Several types of coatings or base metals have also been studied as well, including titanium nitride depositions [4-6] and beryllium copper alloys formed in to vacuum chambers [4,7-9]. The outgassing properties of plasma depositions of silicon have also been studied on two dimensional stainless steel plates [10].

The approach discussed here involves the chemical vapor deposition (CVD) of amorphous silicon on to the surface of three dimensional vacuum system components and chambers. The performance of these components will be evaluated in a controlled manner to comparatively analyze the outgassing characteristics of uncoated substrates vs. coated substrates. The first series of experiments involves the isolated heating and outgassing measurements of comparative parts. The second and most recent evaluation involves the pumping rates of two geometrically identical vacuum chambers attached to the same pump. This second experiment will provide a more applied analysis of the potential advantages imparted by surfaces passivated with an amorphous silicon deposition.

HEAT-INDUCED OUTGASSING COMPARISONS

Theory

By applying a controlled heating rate to a vacuum component, the outgassing rate can be accelerated and easily measured within a reasonable experimental time frame. This can be represented by the following equation [11]:

$$F = [\exp(-E/RT)]t'$$

Where t' is the period of oscillation of a molecule perpendicular to a surface (ca. 10^{-13} sec), E is the energy of desorption (Kcal/g mol), T is temperature and R is the gas constant. By this equation, very slight elevations in substrate temperature will accelerate the outgassing rate exponentially.

Experiment

A vacuum system was constructed to evaluate stainless steel vacuum components symmetrically connected to a common vacuum source. Care was taken by the application of appropriate baffling systems to ensure identical pumping conduction. Figure 1 is a photograph of one of the constructed systems which evaluated the outgassing performance of three metal thimbles with three different surface treatments.

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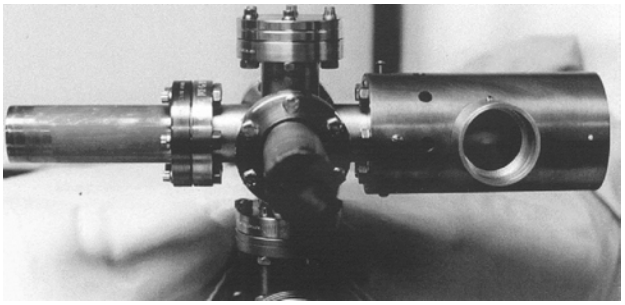

Figure 1. Photo of the vacuum test system for treated metal thimbles.

The vacuum system used a turbo pump to give base pressures in the 10^{-8} Torr range. Pressures were measured with a calibrated hot cathode gauge. Note within Figure 1 on the right side is a heating shroud. This shroud was used to isolate and control the heating process of each thimble in order to individually accelerate and evaluate the outgassing properties of each component. It incorporated appropriate insulation and circulated air cooling so that untreated system components were not subjected to heat conduction from the thimble under evaluation.

The test samples were prepared according to the desired surface type to be measured. One test piece was used as supplied from the manufacturer without surface preparation. The control pieces, label as “heat cleaned”, were exposed to the identical process treatment as the amorphous silicon-deposited pieces. Instead of being exposed to the deposition gases, however, the heat cleaned control parts were exposed to nitrogen gas, thereby not receiving any type of deposition whatsoever. Prior to deposition processing, the heat cleaned and coated components were first cleaned in a multi-bath ultrasonic cleaning system employing a caustic surfactant cleaning agent and subsequent deionized water dragout tanks. Also prior to the actual deposition, these parts were heated in an inert atmosphere to 400°C then in vacuum (ca. 10^{-3} Torr). Amorphous silicon CVD was performed by a proprietary process, called Silcosteel®-UHV [12]. This process is not a line-of-site deposition and results in a complete, conformal 5-10um coating of amorphous silicon on all exposed surfaces (inside and out) of the test component. All evaluated components saw extensive (> 24hr) exposure to standard atmospheric, humidity and temperature conditions prior to connection to the vacuum test system.

The beginning of each experimental setup involved an initial and measured evacuation period. Vacuum was applied equivalently to all components of the system. Base pressure of the system was recorded, then the heat source was applied to an individual test component. At regular timing intervals, the temperature (up to 200°C) and system pressure was recorded, thereby allowing a plot of time (and component temperature at each time mark) vs. change in system base pressure, which is a direct measurement of the component outgassing performance.

Results and Discussion

The first iteration of testing involved three test components. One was used as received from the manufacturer, another was heat cleaned, and a third was treated with an early-generation version of amorphous silicon CVD, called “a-Si 1st Gen.”. This deposition was a thin (ca. 350 Angstrom) coating of amorphous silicon.

Figure 2 shows a plot of time/temperature vs system ΔP in units of 10^{-7} Torr. The system base pressure was 1 x 10^{-7} Torr after 10 hours under vacuum.

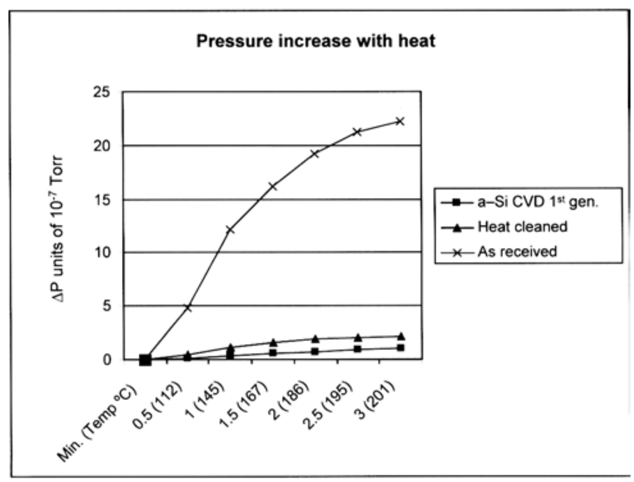

Figure 2. Outgassing Data; First Generation Samples.

The extremely high outgassing rate of the as-received test component clearly overshadows any significant differences in outgassing performance of the other two. The performance of this component resulted in eliminating it from future testing. The remaining measurements of this experimental design included only the test components with an amorphous silicon coating or the heat-cleaned control.

To better illustrate the performance differences of a heat-cleaned part vs. a coated part, the graph in Figure 2 was enlarged (Figure 3).

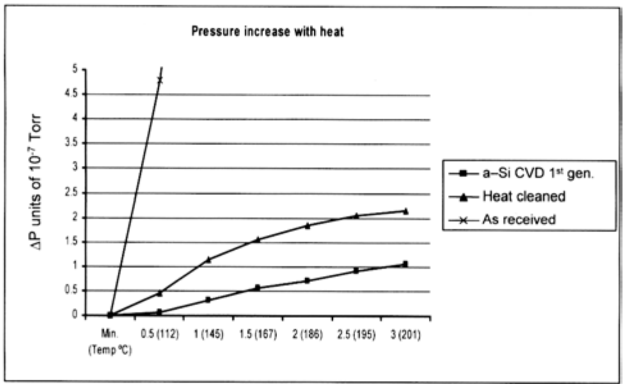

Figure 3. Expanded Y-Scale of Figure 2.

After 0.5 minutes of heating (112°C), the a-Si CVD component displayed a 7.5-fold improvement in outgassing performance over the heat-cleaned test piece (0.06 x 10^{-7} Torr vs. 0.45 x 10^{-7} Torr). The trend of improved outgassing performance of the coated part continued throughout the heating process. This initial result spawned the development of an amorphous silicon deposition process to optimize the outgassing performance of vacuum components.

As improvements were made to the a-Si CVD process, measurements of corresponding improvements in outgassing performance were recorded. Figure 4 plots data of comparative performance between a heat-cleaned test piece vs. “a-Si Coated”.

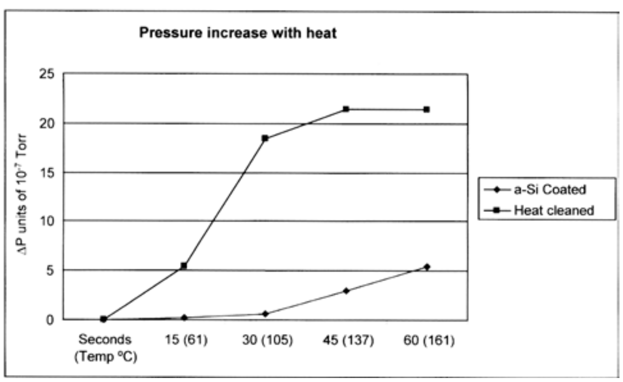

Figure 4. Outgassing data of developed a-Si coating vs. heat-cleaned Control; 1 hour evacuation.

Using a turbo pump, the system was evacuated for 1 hour, giving a system base pressure of 4.6 x 10^{-7} Torr. The heat was then applied individually and alternately to each test piece for one minute (to a maximum temperature of 161°C). The outgassing performance of the coated thimble was superior to the control. The outgassing rate, ΔQ (Torr l sec^{-1} cm^{-2}) can be calculated by multiplying the pressure change by the system conductance and divided by the surface area of the component of interest (the calculated component surface area was 125 cm^2 and the calculated system conductance was 12.5 l/sec). The first data point of 15 seconds (61°C) yielded ΔP values of the heat-cleaned component and coated component of 5.4 x 10-7 Torr and 0.2 x 10-7 Torr, respectively. This gives a ΔQ heat-cleaned value of 5.4 x 10^{-8} (Torr l sec^{-1} cm^{-2}) and a ΔQ a-Si CVD value of 0.2 x 10^{-8} (Torr l sec^{-1} cm^{-2}), or a 27-fold improvement in outgassing performance for the coated component after 1 hour of evacuation.

After 10 hours of evacuation, the heat-cleaned component settled into an identical outgassing performance curve as the a-Si CVD component (Figure 5).

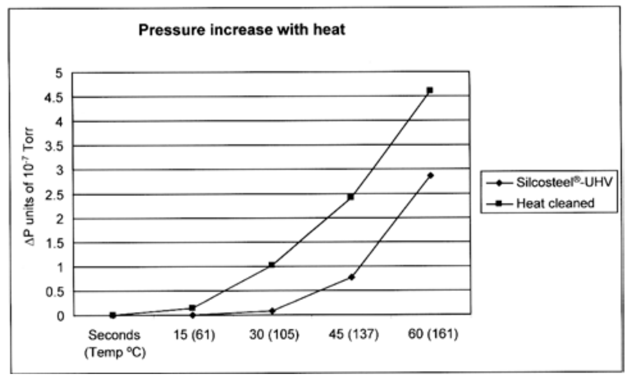

Figure 5. Outgassing Data of Developed a-Si Coating vs. Heat-Cleaned Control; 10 Hour Evacuation.

The outgassing performance, although less disparative than the 1 hour data, still showed a significant improvement of the coated component over the uncoated. The first data point (15 seconds at 61°C) was measured with a base pressure at 7.5 x 10^{-8} Torr. Outgassing rates for the test pieces were as follows: ΔQ heat-cleaned = 0.14 x 10^{-8} (Torr l sec^{-1} cm^{-2}) and ΔQ a-Si CVD = 0.01 x 10^{-8} (Torr l sec^{-1} cm^{-2}), resulting in a 14-fold improvement of the coated vs. uncoated component.

By using an experimental setup applying heat to induce rapid outgassing trends of vacuum components, a comparative illustration of performance was achieved. It became desirable, however, to observe the outgassing performance of an entire vacuum system itself, so that the majority of system surface area was coated with a-Si and compared to a typical untreated system. In order to better simulate a typical production vacuum system, neither test system would be heated, and pressure vs. time plots would better illustrate a more true outgassing performance of a complete vacuum system.

OUTGASSING COMPARISON OF TWO SYSTEMS

Experiment

With so many potential sources of vacuum system contamination, leaks and inaccuracies, such as surface organics, gaskets, valve mechanics, gauge and pump memory effects, and pumping rates of same-model pumps, it is difficult to design a significant and meaningful experiment that accurately compares the outgassing performance of two separate systems. A single system was therefore designed that used a common pump to two symmetrically identical vacuum systems that can be isolated from each other via equivalent valves. Figure 6 is a photograph of the system, where the right chamber is coated with a-Si and the left side is not.

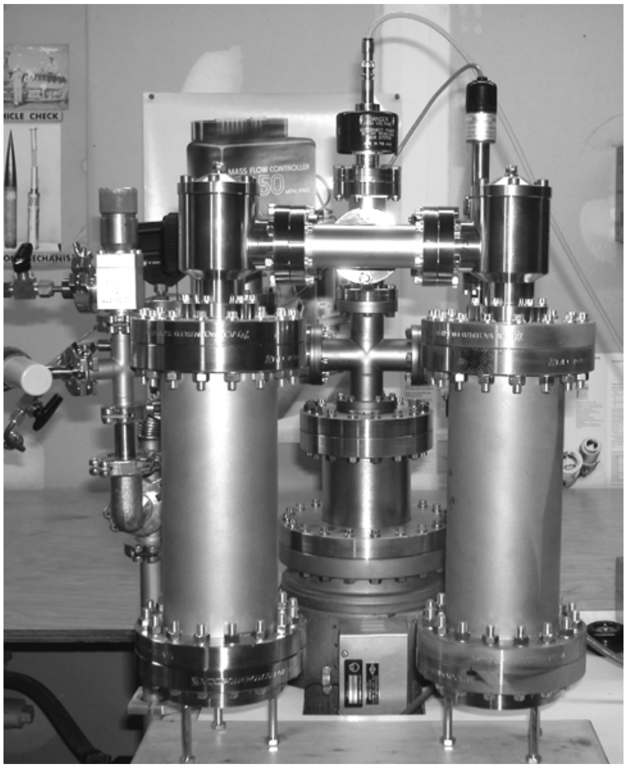

Figure 6. Photograph of comparative test system.

The testing procedure involved the evacuation via turbo pump of the entire system for two hours. Vacuum measurements were made with a Televac 7F cold cathode gauge. Once a base pressure of approximately 10^{-6} Torr was reached, alternating pressure measurements were made. For the first measurement, one side of the system was isolated via one of two all metal angle valves, and the system pressure was noted after 4 minutes. The measure system valve was then closed, a base pressure was noted, then the alternate system valve was opened and pressure noted after 4 minutes. This alternating measurement protocol was followed for a total evacuation time of 2 hours.

Results and Discussion

Figure 7 illustrates the differences in system pressures reached within a given period of time with the same evacuation apparatus. By alternating and isolating pressure measurements of the coexisting systems, a more accurate comparison can be drawn without concern of extraneous contributions to increased system outgassing.

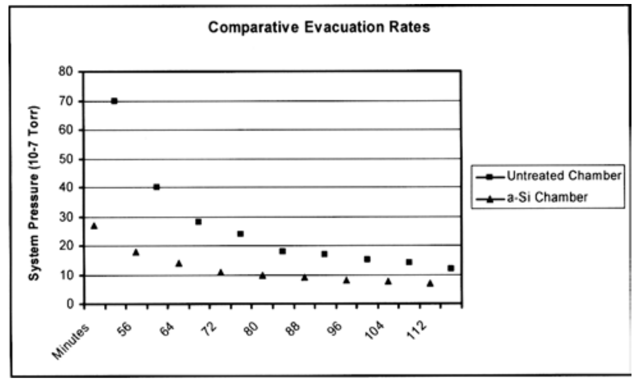

Figure 7. Comparative pressure data for a-Si coated vacuum system vs. untreated vacuum system.

The data presented in Figure 7 is from the first evacuation, and subsequent evacuations will be measured and recorded. Nevertheless, there is a twofold improvement in evacuation rate for the a-Si coated system compared to the untreated system. Consideration of outgassing contributions from downstream uncoated components (i.e. valves and nipples) has not been mathematically eliminated. Therefore, the data presented provides a pessimistic (although advantageous) performance illustration of the a-Si coated chamber. Future data will be reported to complete this body of work.

CONCLUSION

The slow outgassing of water vapor and other contaminants in process vacuum chambers can dramatically hinder evacuation rates, process throughput, and ultimate base pressures. It has been shown that the application of an amorphous silicon deposition throughout the exposed surfaces of vacuum components can dramatically improve outgassing rates and provide an advantage to process chambers that require more rapid and efficient evacuations.

REFERENCES

1. H.F. Dylla, D.M. Manos, and P.H. LaMarche, “Correlation of outgassing of stainless steel and aluminum with various surface treatments,” *J. Vac. Sci. Technol.,* A11 (5), 2623, 1993.

2. Y. Tito Sasaki, “A survey of vacuum material cleaning procedures: A subcommittee report of the American Vacuum Society Recommended Practices Committee,” *J. Vac. Sci. Technol.,* A9 (3), 2025, 1991.

3. J.-P. Bacher, C. Benvenuti, P. Chiggiato, M.-P. Reinert, S. Sgobba, and A.-M. Brass, “Thermal desorption study of selected austenitic stainless steels,” *J. Vac. Sci. Technol.,* A21 (1), 167, 2003.

4. F.L. Tabares, “Thermal and non-thermal surface phenomena and their impact on vacuum,” *Vacuum,* 64, 401, 2002.

5. G. Raiteri and A. Calcatelli, “Thermal desorption from stainless steel samples coated with TiN and oxide layers,” *Vacuum,* 62, 7, 2002.

6. P. He, H.C. Hseuh, M. Mapes, R. Todd, D. Weiss, and D. Wilson, “Outgassing properties of the spallation neutron source ring vacuum chambers coated with titanium nitride,” *J. Vac. Sci. Technol.,* A22 (3), 705, 2004.

7. T. Oishi, Y. Konishi, M. Goto, A. Kasahara, M. Tosa, and K. Yoshihara, “Control of Pressure rise in a vacuum chamber by boron nitride and copper composite coating,” *J. Vac. Sci. Technol.* A21 (6), 1873, 2003.

8. F. Watanabe, “Extremely low-outgassing material 0.2% beryllium copper alloy,” *J. Vac. Sci. Technol.* A22 (1), 181, 2004, and “Erratum: Extremely low-outgassing material 0.2% beryllium copper alloy,” *J. Vac. Sci. Technol.* A22 (3), 739, 2004.

9. C. Dong, P. Mehrotra, and G. R. Myneni in *Methods for reducing Hydrogen Outgassing*, G.R. Myneni and S. Chattopadhyay Eds.; Hydrogen in Material and Vacuum Systems; American Institute of Physics: Melville, NY, 307, 2003.

10. S.S. Inayoshi, S. Tsukahara, and A. Kinbarra, “Decrease of water vapor desorption by Si film coating on stainless steel,” *Vacuum,* 53, 281, 1999.

11. A. Roth; *Vacuum Technology*, Elsevier Science Publishers, Amsterdam, 2nd ed., 177, 1982.

12. Restek Corporation, Bellefonte, PA.