HIGH TEMPERATURE OUTGASSING TESTS ON MATERIALS USED IN THE DIII–D TOKAMAK

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ABSTRACT

This paper is a continuation of previous work on determining the outgassing characteristics of materials used in the DIII-D magnetic fusion tokamak [K.L. Holtrop, J. Vac. Sci. Technol. A **17**, 2064 (1999)]. Achievement of high performance plasma discharges in the DIII-D tokamak requires careful control of impurity levels. Among the techniques used to control impurities are routine bakes of the vacuum vessel to an average temperature of 350°C. Materials used in DIII-D must not release any impurities at this temperature that could be transferred to the first wall materials and later contaminate plasma discharges. To better study the behavior of materials proposed for use in DIII-D at elevated temperatures the initial outgassing test chamber was improved to include an independent heating control of the sample and a simple load-lock chamber. The goal was to determine not only the total degassing rate of the material during baking but to also determine the gas species composition and to obtain a quantitative estimate of the degassing rate of each species by the use of a Residual Gas Analyzer. Initial results for aluminum anodized using three different processes, stainless steel plated with black oxide and black chrome, and a commercially available fiber optic feedthrough will be presented.

I. INTRODUCTION

The DIII-D tokamak [1] is a device used for plasma fusion research where high performance can only be achieved if impurities are carefully controlled. For high Z ($Z \geqq 20$) materials, impurity fractions as low as 10^{-3} can have a considerable negative effect on the plasma. For DIII-D operational parameters this implies that the total high Z impurity levels in the plasma should remain below 2×10^{-6} moles or 1.7×10^{-2} Torr-liter. An example of this low level requirement and the need for material degassing tests can be highlighted by an incident that occurred in 1990. Plasma performance was degraded by an unknown source of bromine. The bromine source was traced to the hole reinforcements on a small paper tag that was inadvertently left in the tokamak during a vent.

When an assembly is proposed for use in DIII-D it is required that all materials be listed to verify that no prohibited high Z/low vapor pressure elements are present. Occasionally, a commercial product is proposed which contains "vacuum-grade" epoxies, plastics or similar material where either the elemental make-up is unknown or there are questions about the material's vacuum properties when heated. Whenever possible the material is analyzed using methods such as secondary electron microscope (SEM) and energy dispersive x-ray (EDX) analysis to determine the elemental make-up. However, it is not always possible to access the suspect material without destroying the assembly.

There is an additional constraint on materials used in DIII-D. In order to condition the machine for plasma operations the machine is routinely baked. There is a considerable variation in temperature in individual parts of the machine but even recessed ports can rise to above 200°C while inside wall components are baked to nearly 400°C. Individual baking sessions typically range from 8 to 16 hours, but occasionally can last up to 40 hours. For 2004 there was a total of 252 hours of baking. Materials used in DIII-D must remain stable and have low degassing rates at these elevated temperatures.

An outgassing station had been built and used in a previous study to determine the room temperature outgassing characteristics of graphite, Grafoil®, and MgO coaxial cable [2]. This station was modified for high temperature degassing tests. A low cost commercial quadrupole residual gas analyzer (RGA) was used as the impurity detection tool. The goal was to determine whether the performance of this RGA could be quantified enough to provide definite answers to whether proposed materials could be allowed in the DIII-D vessel. Initial tests were run on a commercially available fiber optic feedthrough, various anodized aluminum samples, and stainless steel samples with a black oxide or black chrome finish. The results from these tests will be presented and the challenges in analyzing the RGA data will be discussed.

II. OUTGASSING STATION

The degassing tests were performed in an 18 ℓ stainless steel vacuum chamber which has a surface area of approximately 9.0×10^3 cm^2 (Fig. 1). Through the use of heater cables, thermocouples and temperature controllers the walls of the entire chamber could be independently raised to 400ºC. After initial testing the walls were maintained at 100ºC to minimize the effect of wall pumping. A load lock chamber with a pneumatically controlled valve was installed on one side of the chamber. A movable cart slid along rails from the load lock chamber and onto a heater plate in the outgassing chamber. The bulk of the cart was made of stainless steel, while the bottom of the cart was made out of an aluminum alloy. Once inserted a thermocouple on a linear feedthrough could be extended to measure the temperature of the sample placed in the cart. The heater plate consisted of a heater wire sandwiched between foam copper sheets, which were sandwiched between stainless steel plates. The heater wire was composed of nickel-chrome wire electrically isolated from a stainless steel sheath by MgO. The heater plate had a temperature controller with feedback from a thermocouple attached to the plate and could be raised up to approximately 750ºC.
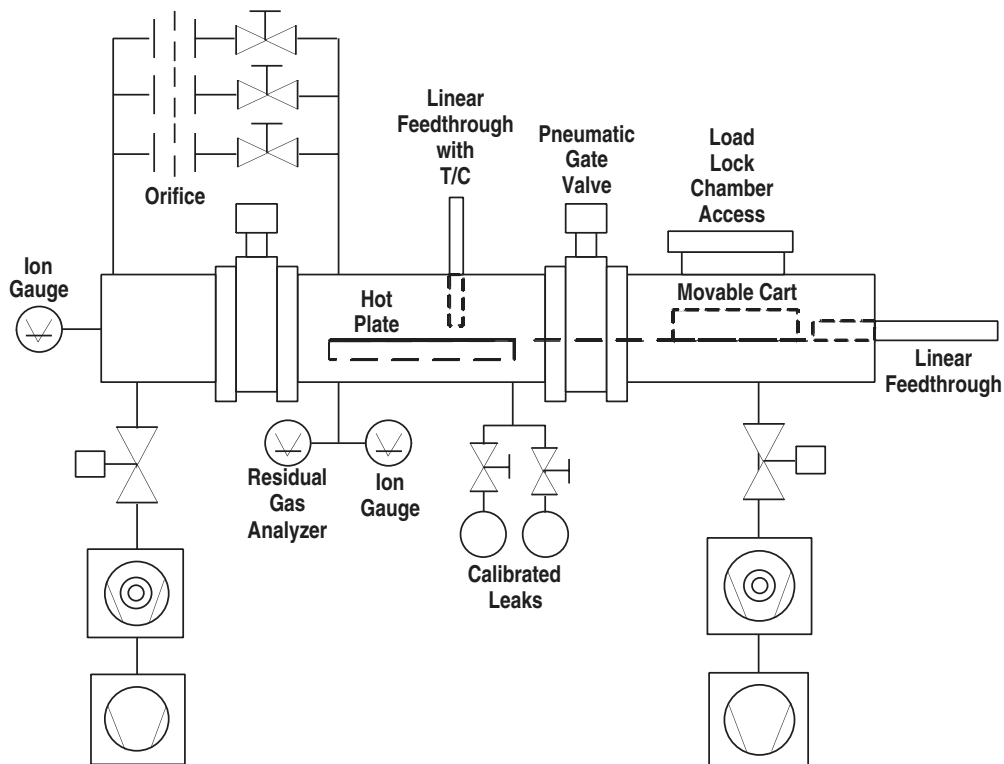

Fig. 1. Schematic of the outgassing station.

Pumping was supplied by a 330 ℓ/s turbo-molecular pump isolatable from the chamber by a pneumatically controlled valve. This main valve could be closed and a smaller conductance achieved through the use of smaller manual bypass valves. Bayard-Albert ion gauges were installed on both the main chamber and the outgassing chamber so the throughput method could be used to quantitatively estimate the degassing rate. Calibration of the conductances of both the main pumping path and the pumping path through the smaller valves was accomplished using calibrated leaks. An RGA was installed on the sample chamber to determine the gas species being desorbed.

The diagnostic and control interface to the outgassing system used a Linux computer with a custom written C program that made use of the Kylix® software package for graphics. The Linux computer communicated through an Ethernet connection to a programmable logic controller (PLC), which acquired the pressure and temperature data, and to the RGA through a RS-232/Ethernet adapter. The C program created an unified interface that polled both the RGA and the PLC for data, and then archived the data to both a local disk and also to a Microsoft SQL database server for further analysis. One of the goal of the tests was to see if a set of metrics could be developed that could then be coded to run automatically and thereby reduce post test analysis time.

III. RGA ANALYSIS

A standard quadrupole RGA was installed to determine the various degassed gas species. To determine if the RGA has the proper sensitivity to detect impurity levels that could affect plasma performance a worst case scenario was assumed. It was assumed that the all the impurity gas desorbed from a baking session did not pump out, but instead was reabsorbed onto a cooler surface and then subsequently desorbed during a plasma discharge. For a material to degas 1.7×10^{-2} Torr-liter of material (the level which could degrade plasma performance) from a typical DIII-D bake lasting eight hours (2.88×10^4 s) a material would have to have a degassing rate of 5.9×10^{-7} Torr-liter/s. For the large conductance opening on the outgassing station, which has an effective pumping speed of ~ 200 ℓ/s, this would correspond to a partial pressure in the low 10^{-9} Torr range. For the smaller conductance with an effective pumping speed of ~ 4.5 ℓ/s this would correspond to a partial pressure in the 10^{-7} Torr range. Both of these values are within the usable range of the RGA.

The usually stated method of analyzing RGA data to obtain quantitative results is to use multiple linear regression analysis to solve the system of equations given by

$$i_{\mathrm{m}} = \sum_{\mathrm{g}}(S_{\mathrm{g}}\alpha_{\mathrm{mg}})p_{\mathrm{g}} \quad , \tag{1}$$

where i_{m} is the ion current at mass m in Amperes, S_{g} is the RGA's partial pressure sensitivity for gas g in Amperes/Torr, α_{mg} is the fragmentation factor of gas g at mass m, and p_g is the partial pressure for gas g in Torr. To solve Eq. (1) for the quantities p_g, both S_{g} and α_{mg} must be known. However, for almost all spectra of interest these values were not known. For the complex hydrocarbons that are often generated on the hot surfaces it is uncertain even what gases and factors to use. Efforts at solving Eq. (1) using various estimates for the proper factors did not yield consistent or physically realistic results.

Instead of this approach a rough calibration of the RGA was performed by summing up all the peaks and dividing this into the total pressure as measured by a Bayard-Albert gauge. This provided an order-of-magnitude estimate for the partial pressure levels for the majority of gas species.

Readsorption is known to significantly affect outgassing rate measurements and corrections to the measured rate have been discussed by Hobson [3]. The true outgassing rate, q_{t}, is the sum of the measured rate obtained from standard throughput measurements, q_{m}, plus the amount pumped by the wall, $q_{\mathrm{w}} = fAs$, where f is the molecular flux to the wall, A is the surface area of the walls, and s is the sticking fraction. This can be expressed as

$$q_{\mathrm{t}} = q_{\mathrm{m}} + fAs = q_{\mathrm{m}} + \frac{10^3}{\sqrt{MT}} \, sP_v A \; (\mathrm{Torr} * \ell * \mathrm{s}^{-1} * \mathrm{cm}^{-2}) \quad , \tag{2}$$

where M is the AMU of the gas, T is the temperature in K, P_v is the pressure in the main chamber in Torr, and A is the area of the main chamber in cm.

Modulating the conductance from the sample chamber to the pumping chamber has been used to compensate for chamber wall effects [4]. From Moraw [5] the sticking fraction, s, can be determined by changing the conductance between two known conductances, G_1 and G_2, measuring the pressure on the vessel side where the sample is located, p_{v1} and p_{v2}, and on the pumping side p_{p1} and p_{p2} for the two cases. Assuming that q_t is the same for both these cases, and then solving for s to obtain

$$s = \frac{G_1(p_{v1} - p_{p1}) - G_2(p_{v2} - p_{p2})}{\dfrac{10^3}{\sqrt{MT}}(p_{v2} - p_{v1})A} \quad . \tag{3}$$

For the current tests the RGA was installed only on the vessel side. As a further simplification it is assumed that the orifice is sufficiently restrictive so that $p_v > p_p$, so that s reduces to

$$s = \frac{G_1 p_{v1} - G_2 p_{v2}}{\dfrac{10^3}{\sqrt{MT}}(p_{v2} - p_{v1})A} \quad . \tag{4}$$

This yields an upper limit estimate of the sticking fraction for a particular partial pressure using only the RGA on the main outgassing chamber. Results for Eq. (4) will be discussed in Section IV which discusses the fiber optic feedthrough tests.

To properly obtain an estimate for the sticking fraction a RGA would also need to be installed on the pumping chamber. In order to effectively use this conduction modulation technique the control system would need to be upgraded for automatic cycling of the conductance valves and the computer code expanded to calculate the sticking fractions and also to properly identify and archive all the data.

IV. FIBER OPTIC FEEDTHROUGH

The first item tested was a commercial vacuum fiber optic feedthrough obtained from Fiberguide Industries. The feedthrough assembly consisted of seven glass fibers wrapped in "natural" Silverflex (a woven fiberglass textile) and then encased in a stainless steel sheathing. These lines are bundled together and fed through a tube that penetrates a standard 6.99 cm. Conflat[®] sealed vacuum flange. The vacuum seal between the stainless steel encased fiber lines and tube is accomplished through the use of a silver epoxy. This feedthrough was installed on the chamber and then heated with heater tapes up to 250ºC, which is the maximum rated temperature of the epoxy in the feedthrough. The RGA spectra showed unusually high levels of mass 29 (Fig. 2) and mass 79 (Fig. 3). A study on Nextel[®] (a comparable woven fiberglass textile) looking in the 0-50 AMU range found similar peaks that were attributed to complex hydrocarbons [6]. The peak at 79 is unidentified. It could indicate bromine, however, the two isotopes of bromine, ^{79}Br and ^{81}Br occur in roughly equal measure and the peak at AMU 81 is a factor of 10 too small. It is possibly a hydrocarbon but there is not the complex pattern usually associated with a hydrocarbon. The mass 29 and mass 79 levels decreased rapidly after the bake started and within a couple of hours could no longer be detected on the RGA. The same feedthrough was subsequently baked again to 250ºC with no reoccurrence of mass 29 or 79.
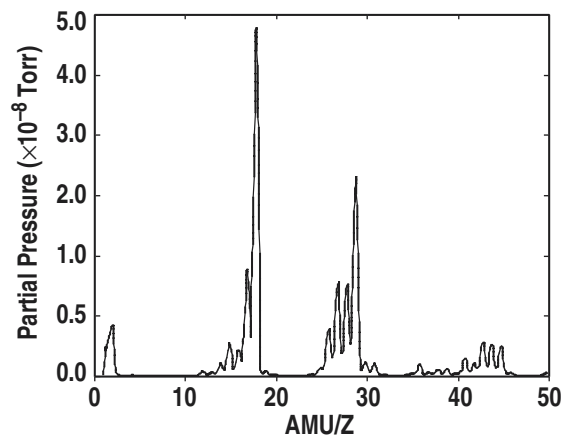

Fig. 2. RGA scan of the fiber optic feedthrough at 250ºC for AMU/Z 1-50. The mass 29 level is higher than the mass 28 peak (N_2).

The value of the sticking fraction, s, using Eq. (4), and the ratio of the flux absorbed on the wall, q_{w}, obtained from Eq. (2) to the measured outgassing ratio, q_{m}, obtained from the throughput method were estimated with the chamber wall temperature at 23ºC (room temperature), 100ºC and 200ºC (Table I). The conductance used for these calculations was the calibrated N2 conductance value with a $\sqrt{28/Mass}$ factor to compensate for differences in the

atomic mass. For these tests, which used large samples and had a corresponding high total outgassing rate, *i.e.* in the 10^{-4} Torr-liter/second range, the effect of the sticking fraction is moderate at room temperature. The sticking fraction was reduced by approximately a factor of ten for most gas species when the wall temperature was raised to 100ºC from room temperature. Very little further reduction in the sticking fraction was achieved by continuing to raise the wall temperature to 200ºC.
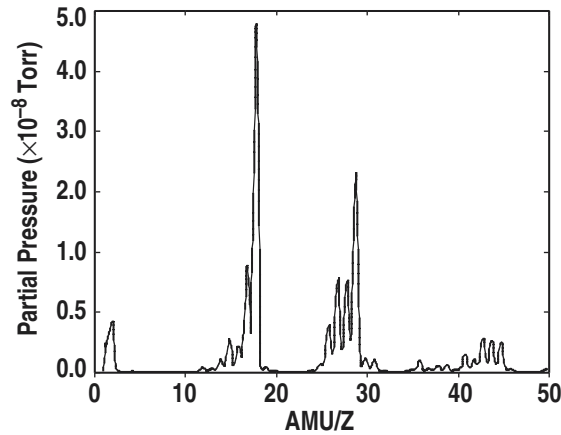

Fig. 3. RGA scan of the fiber optic feedthrough at 250ºC for 51-100 AMU/Z. The large peak at mass 79 could not be identified.

Table I. The sticking fraction, s, and the ratio of the flux adsorbed on to the wall, q_w, to the measured outgassing rate, q_m. The wall pumping effect was reduced about a factor of 10 by heating the chamber walls to 100ºC. Further heating to 200ºC yielded a much smaller reduction in the sticking fraction.

Mass	s (23ºC)	q_w/q_m (23ºC)	s (100ºC)	q_w/q_m (100ºC)	s (200ºC)	q_w/q_m (200ºC)
18	7.4×10^{-4}	0.11	9.6×10^{-5}	0.012	8.0×10^{-5}	0.010
28	1.9×10^{-4}	0.028	2.3×10^{-7}	2.4×10^{-5}	-1.7×10^{-5}	-0.002
29	2.1×10^{-4}	0.32	3.3×10^{-4}	0.042	2.2×10^{-4}	0.028
80	8.0×10^{-4}	1.2	3.9×10^{-4}	0.049	3.4×10^{-4}	0.043
Total	2.2×10^{-4}	0.032	3.0×10^{-5}	0.004	2.2×10^{-5}	0.003

V. BLACK OPTICAL FINISHES ON METAL

Occasionally, there is a need to optically darken a metal surface to lower unwanted light scattering and reflection. There are a variety of different finishes available to darken both aluminum and stainless steel. These finishes seemed like good candidates for the initial degassing tests as the elemental make-up could be determined beforehand, which could then be compared to the results from the tests. Tests were performed on three different varieties of anodized aluminum and on two varieties of coated stainless steel.

Initial tests of the materials in the load lock chamber cart had background impurity gases that were traced to the aluminum alloy bottom of the cart. There were large increases in mass 24 (Mg) starting at approximately 415ºC, and mass 64, 66, and 68 (Zn) starting at approximately 620ºC. Both these elements are constituents of the aluminum alloy used for the cart bottom. The load lock cart was not used in subsequent tests and the entire chamber was vented with a continuous N_2 purge when the test samples were inserted into the chamber and directly onto the hot plate. The test samples were flat 7.62 cm x 8.08 cm sheets with the blackening finish applied to both sides. After insertion of the sample the chamber was pumped on for approximately 24 hours with the chamber at 100ºC before the high temperature degassing tests began. For the degassing tests the hot plate was slowly ramped at 150ºC per hour until the sample temperature on the upper face reached 400ºC.

A. Aluminum

The aluminum was anodized by three different methods: chromic Type 1 Class 2, hard Mil-A-8625F, and sulfuric Mil-A 8625F. Using an SEM and EDX analysis the elemental makeup of each of the coatings was obtained (Table II).

Table II. Elemental makeup in atomic content percentage for the anodized aluminum. Of particular concern is the sulfur which has a low vapor pressure.

Kind/%	O	Al	C	S (%)	Mg	Ni	<0.4%
Sulfuric	64.9	17.0	15.7	2.0	0.2	0.1	Cr
Hard	66.6	18.2	11.9	2.9	0.2	0.1	Fe
Chromic	64.6	15.6	18.5	0.4	0.2	0.2	Cr, P, SiC

The main concern over the use of the anodized aluminum finishes in the DIII-D tokamak has been the possibility of sulfur being degassed during a bake. An RGA spectrum for the degassing test of the sulfuric finish shows sulfur as indicated by ^{32}SO (mass 48), ^{34}SO (mass 50), ^{32}SO$_2$ (mass 64), and ^{34}SO$_2$ (mass 66) (Figs 4 and 5). These RGA spectra also show the difficulties in

interpreting the data. As would be expected a hot porous surface with C, O, and H_2O generates a large amounts of hydrocarbons. These hydrocarbons are not of concern being composed of low Z elements. However, they could easily mask the presence of other higher Z elements.

There is a large increase in the sulfur level, as indicated by mass 64 data, for all the anodized finishes when the sample reaches 250°C (Fig. 6). After achieving steady state temperature at approximately 400°C there is a continuous decrease in the mass 64 level. This would indicate that the sulfur could be removed from the films by continued baking. The chromic finish which had the lowest sulfur from the SEM/EDX analysis also had the lowest mass 64 degassing rate. However, it was the only sample that was affected by the bakeout; it changed color from black to a copper-brown during the baking.
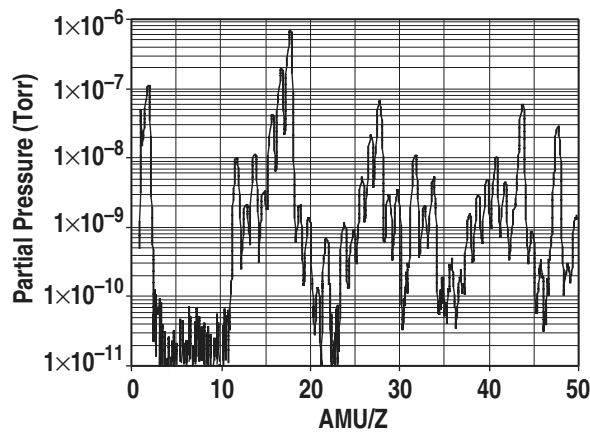

Fig. 4. RGA scan of sulfuric anodized aluminum finish at 350°C. Sulfur is present as ^{32}SO (mass 48) and ^{34}SO (mass 50). Water is present (mass 18, 17, 16) as are RGA artifact peaks, mass 44 (CO_2), mass 32 (O_2), mass 12 (C), as well as many suspected overlapping hydrocarbons making analysis difficult.
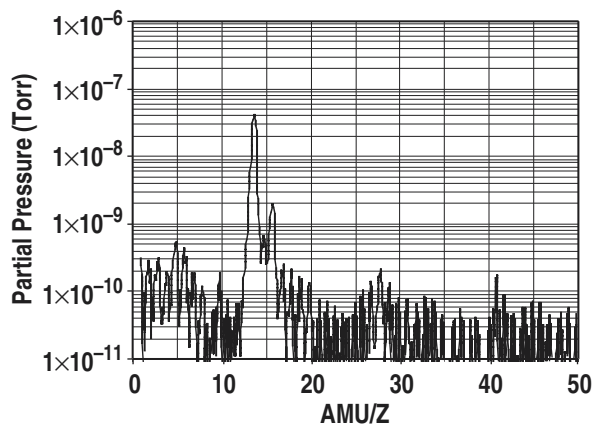

Fig. 5. RGA scan of a sulfuric anodized aluminum finish at 350°C. Sulfur is clearly present as ^{32}SO$_2$ (mass 64) and ^{34}SO$_2$ (mass 66).
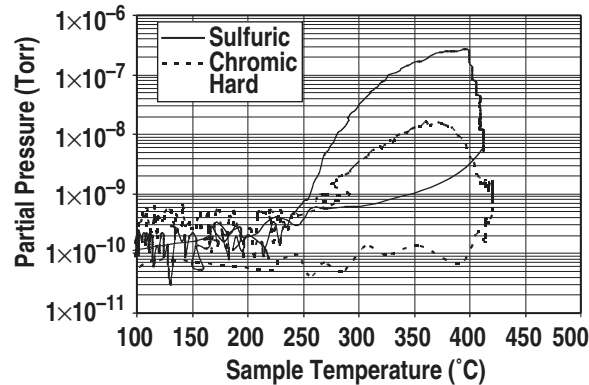
Fig. 6. Evolution of mass 64 ($^{32}SO_2$) with temperature. At around 250ºC there is a marked increase in its degassing rate. The level begins to drop after reaching steady state temperature. It may be possible to bake all the S out with a sufficiently long bake.

B. Stainless steel

The next materials tested were black chrome and black oxide finishes on stainless steel. The elemental make-up was determined using SEM/EDX (Table III).

Table III. Elemental makeup in atomic content percentage for the black chrome and black oxide finish on stainless steel. Of concern are the fluorine in the black chrome and the sulfur in the black oxide.

Kind/%	O	C	Cr	Fe	F	Ni	Al	S	Na	<0.4%
Chrome	56.8	24.1	13.6	0.0	4.7	0.0	0.0		0.8	
Oxide	56.2	18.0	0.0	15.3	0.0	2.3	2.4	1.6	0.7	Si, K

For the black chrome finish a concern was the high fluorine levels. Like bromine, fluorine is highly reactive and tends to recycle in the vessel as opposed to being pumped out. However, there was no indication of fluorine at mass 19 (F) or mass 20 (FH) in the RGA spectrum during the degassing test. At the beginning of the bake there was some small level of suspected hydrocarbons that quickly disappeared. An RGA spectrum after several hours of baking showed no impurity levels at all (Fig. 7).

For black oxide finish the main concern was the sulfur. The RGA spectra for the degassing test was very similar to the black chrome finish with the exception that sulfur at the same peak locations as for the anodized aluminum was observed. Following bakeout the finish was noted to have lightened to a dark grey.

C. Total evolved gas

For a final comparison the total evolved gas quantity (Torr-liter) for each finish was measured using the throughput method. This was done for the twenty-four hour pump-down period starting ten minutes after the chamber was first evacuated and for the first five hours of the bake test (Table IV). For comparison the results from the load-lock chamber cart, a single

graphite tile and a Grafoil® gasket are also shown. The DIII-D vessel is lined with several thousand of these graphite tiles, each with it's own gasket, that act as the plasma facing surface. None of the finishes would appreciably lengthen the pump-down process of DIII-D if used in moderation.
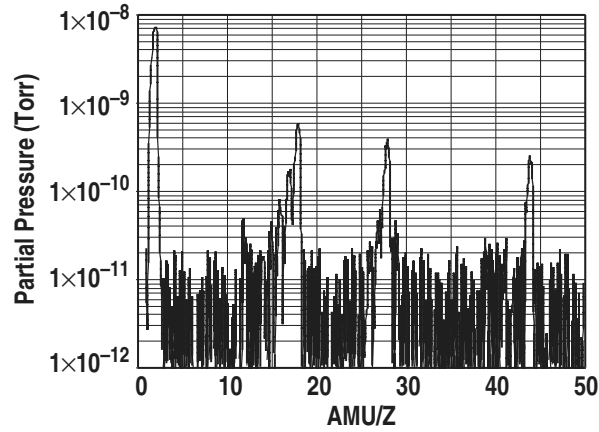

Fig. 7. RGA scan of black chrome at 400ºC after several hours of baking. There are no signs of any impurities including fluorine that is present in the finish.

Table IV. The total evolved gas for all the anodized aluminum and stainless steel samples. The results for the empty outgas cart and for a typical graphite tile and Grafoil Gasket® which cover the DIII-D vessel walls are shown for comparison

Material	24 h Pumpdown (Torr-ℓ)	5 h Bake (Torr-ℓ)
Chamber (with cart)	1.1	1.1
Graphite tile	12.4	20.3
Grafoil gasket®	2.5	1.1
Sulfuric (Al)	15.5	14.3
Chromic (Al)	-	17.3
Hard (Al)	32.3	20.8
Black chrome (SS)	1.5	3.1
Black oxide (SS)	1.1	1.2

V. CONCLUSION

An outgassing station was improved to perform high temperature (up to 400°C) degassing tests. To determine the degassed gas species a low cost commercially available quadrupole RGA was installed on the sample chamber. Tests on a commercial feedthrough, three types of anodized aluminum, and two types of blackened stainless steel were performed. The commercial feedthrough displayed several unknown peaks that eventually disappeared after several hours of baking at 250°C. All the anodized aluminum samples degassed sulfur during baking though it may be possible to completely degas the sulfur with a sufficiently long bake. The stainless steel samples had much cleaner RGA spectra; however the black oxide finish also degassed sulfur and discolored during the baking. The stainless steel with a black chrome finish would be the preferred option for use in DIII-D; SEM/EDX analysis showed fluorine in the film but none was present in the RGA spectrum.

To extract rough order-of-magnitude estimates using the RGA took considerable effort. The effect of the sticking fraction, which was estimated by switching between conductance paths, was moderate at room temperature. By raising the wall temperature from room to 100°C the sticking fraction was reduced by approximately a factor of ten and became negligible. Very little additional reduction of the sticking fraction was seen when the wall temperature was increased to 200°C. A better estimate of the sticking fraction could be obtained by installing an RGA in the pumping chamber as well as the sample chamber.

REFERENCES

[1] J.L. Luxon, Nucl. Fusion **42**, 614 (2002).

[2] K.L. Holtrop, J. Vac. Sci. Technol. A **17**, 2064 (1999).

[3] J.P. Hobson, J. Vac. Sci. Technol. **16**, 84 (1979).

[4] K. Saito, Vacuum **47**, 749 (1996).

[5] M. Moraw and H. Prasol, Vacuum **49**, 353 (1998).

[6] S. Sinharoy, J. Vac. Sci. Technol A **8**, 930 (1990).

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