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INFLUENCE OF OXYGEN AND WATER VAPOUR ON THE ION INDUCED DESORPTION
FROM STAINLESS STEEL

by

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ABSTRACT

Ion induced neutral gas desorption, residual gas composition and pumpdown times were measured after one hour exposures of a stainless steel tube (SS 304 L) to the following atmospheres (atmospheric pressure) :

- (a) pure N₂
- (b) normal air
- (c) pure 80% N₂, 20% O₂ mixture
- (d) pure N₂ with the system open during the exposure

It is shown that exposure to oxygen containing atmospheres increases the subsequent ion induced desorption of CO, CH₄ and CO₂ while the H₂ desorption is reduced. Exposure to water containing atmospheres, on the other hand, stimulates the ion induced desorption of all the four commonly desorbing species (CO, H₂, CH₄ and CO₂).

The effects on the ion induced desorption and residual gas composition of an exposure to ordinary air is shown to be attributed mainly to its water vapour content. It is shown that if filaments (ion gauges, etc.) are on during low pressure oxygen exposures, the ratio between the ion induced desorption of CO and CO₂ will be affected, probably due to the formation of excited oxygen molecules at the filaments.

Backfilling the vacuum system with pure N₂ before opening to air is shown to give a considerable decrease in surface contamination, which is seen from the ion induced desorption response as well as the reduced evacuation time.

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1. INTRODUCTION

The desorption of adsorbed species from the vacuum envelope is normally the limiting factor for the vacuum performance of an UHV system. In systems where the wall is subjected to particle bombardment, as in proton storage rings or fusion devices, the importance of the wall conditions is even further stressed, as the energy transfer to the wall will allow contaminating molecules trapped in comparatively deep binding states to be desorbed into the gas phase^{1,2}). Recent work has made it increasingly clear that complex chemical processes take place at the near surface layer of vacuum chamber materials. These processes play a crucial role in determining which molecules are formed at the surface, and are subsequently available for desorption^{3,4}). At the Intersecting Storage Rings (ISR) at CERN, Geneva, the interest has for a long time been focussed on the phenomenon of ion bombardment induced neutral gas desorption as the vacuum performance, and thus the maximum proton current that can be stored, is closely linked to this process^{5,6,7,8}).

In a previous work dealing with stainless steel 304 L, it was shown, using isotopically marked gases, that the adsorption-desorption mechanism frequently involves dissociation of the adsorbed molecule and the subsequent incorporation of the fragments in the desorbed molecule³). It was also shown that for exposures to 1×10^{-5} torr for 2 h, the influence on the desorption coefficients was far greater in the case of either oxygen or water vapour exposure than for any of the other gases studied.

In this paper, the investigation of the effects of gas exposure on the ion induced neutral gas desorption from stainless steel 304 L has been extended to higher exposures (1 - 760 torr for 1 h), and the attention has been focussed on the influence of atmospheres containing water and oxygen. The effects of the exposures on the general vacuum behaviour, defined by residual gas composition and pumpdown times, were also investigated and those data were correlated with the results for the ion induced desorption.

2. EXPERIMENTAL

2.1 Vacuum System

The experimental apparatus has been described elsewhere³) and will only be presented briefly here.

The stainless steel vacuum system consisted of a 5 m long tube, 5 cm in diameter, pumped with ion pumps and Ti sublimation pumps at each end, giving a base pressure after bakeout of approximately $2 \cdot 10^{-11}$ torr, see fig. 1. A quadrupole mass spectrometer (Balzers QMG 511) was mounted at the midpoint of

the tube. A titanium wire, connected to the outside through electrical feedthroughs, was stretched along the centre of the tube. An electron source, consisting of a screened tungsten filament was mounted at the tube midpoint. In order to obtain ion bombardment of the chamber surface, the system was backfilled dynamically to $9 \cdot 10^{-6}$ torr of argon while biasing the wire positively (+ 520 V). With this geometry, electrons generated at the filament will be trapped in orbits around the wire which extend the whole length of the tube (orbitron configuration) and produce Ar^+ ions that will be repelled by the wire and thus accelerated onto the wall. By measuring the increase in partial pressures with the mass spectrometer, the desorption coefficients (η -values), defined as the number of desorbed molecules per impinging ion, could be calculated. The effective pumping speed in the system that had to be known in order to calculate the η -values, could be derived from the geometry of the system as the pumping speed of the activated Ti-sublimation pumps at the ends of the tube was high compared to the conductance of the tube (conductance limitation). To calculate the η -values for methane, which is poorly pumped by sublimation pumps, it had to be taken into account that this gas was pumped mainly by the turbomolecular pump used to keep the argon flowing during the measurement. A detailed description of the calculation procedure is given in ref. 3.

The contribution to the partial pressure increases due to electron induced desorption at the central wire was negligible for CO , CO_2 and CH_4 , but had to be corrected for in the case of H_2 .

2.2 Measurement Procedure

All gas exposures were preceded by a 275°C bakeout of the complete system for at least eight hours in order to obtain a well defined starting condition. The effect on the ion induced desorption when exposing a baked stainless steel surface to different atmospheres is reversible, i.e. a subsequent bakeout brings back the desorption coefficients to their original values. After many bakeout cycles, however, those 'base η -values' tended to decrease, indicating a slow cleaning of the surface. After the bakeout the η -values were measured (' η after bake' denoted B in the figures), followed by the desired gas exposure. If not otherwise stated, the exposures lasted for one hour and before going up to final pressure, a mass spectrum was recorded at $1 \cdot 10^{-5}$ torr to check the purity of the gas.

The pumpdown curve was recorded for the first forty minutes of the evacuation and a mass spectrum was recorded after 23 hours, followed by a

measurement of the η -values (' η after exposure'). Except for the air and water vapour exposure, high purity (better than 99.99%) gases supplied by Carbagas were used.

2.3 Pretreatment of the tube

Previous to all measurements the 5 m long test section had been subjected to the normal ISR cleaning procedure involving chemical solvent cleaning followed by a vacuum anneal. The chemical cleaning is done in four steps : 1. Vapour degreasing in perchloroethylene (C_2Cl_4), 2. ultrasonic cleaning in alkaline detergent (pH=11), 3. rinsing in cold demineralized water, 4. drying in a hot air oven at 150°C. The subsequent vacuum anneal is done in an industrial vacuum furnace for 2 hours at 950°C and at a pressure of less than 1.10^{-5} torr. In addition, the test section went through the chemical cleaning procedure once more before being mounted and baked in-situ.

3. RESULTS

3.1 Exposure to N_2 Atmospheric Pressure

Earlier results³⁾ indicate that the interaction between nitrogen and a stainless steel surface is negligible. To check if this is valid also for high pressure exposures (atmospheric pressure) and if it is possible to handle large quantities of gas without getting an influence from the residual contamination, a one hour exposure to nitrogen was made at atmospheric pressure. The effect of this exposure on the ion induced desorption is shown in Fig. 2 and the pumpdown curve after the exposure is given in Fig.3 (curve a).

The small effect on the η -values as well as the quick pumpdown indicates that the interaction with the vacuum chamber surface was negligible and also suggests that the level of residual contamination of H_2O and O_2 was small. The mass spectrum recorded 23 h after the initialization of pumpdown (total pressure $5.9.10^{-10}$ torr) is not so different from that normally found in a baked stainless steel UHV system, see Fig. 4a.

3.2 Exposure to Laboratory Atmosphere

As can be seen from Fig. 2, the air exposure gives a dramatic increase in the desorption coefficients for all four desorbing species (CO , CO_2 , H_2 and CH_4). The pumpdown curve (Fig. 3 curve b) as well as the mass spectrum recorded 23 h after the exposure (fig. 4b), show clearly the typical and well known characteristics of an unbaked vacuum system, i.e. slow evacuation and a high mass 18 signal. Comparing the effect of the atmospheric air exposure on the

η -values with that of a 1.10^{-5} torr, 2 h, H_2O exposure (Fig. 2) reveals striking similarities suggesting that water vapour plays a dominating role in creating the observed effects.

3.3 Exposure to Oxygen and Oxygen Nitrogen Mixture

As can be seen from Fig. 2, the effect on the ion induced desorption of a one torr O_2 exposure lasting one hour, is qualitatively different from the effect of the air exposure in that the desorption of hydrogen has decreased after the oxygen exposure.

In order to separate the effects on the surface layer created by water vapour with those from oxygen, a high purity mixture of nitrogen and oxygen ('artificial dry air') was injected into the system at atmospheric pressure. The effect on the η -values showed the same features as those of the oxygen exposure (note the decrease in η_{H_2}) and, as can be seen from the pumpdown curve (fig. 3, curve c), the evacuation is somewhat slower than after the exposure to pure nitrogen.

The mass spectrum taken after 23 hours of pumping (fig. 4c) is significantly different from the spectra typical for a baked system (fig. 4a) or a system exposed to atmosphere (fig. 4b). Compared to the spectrum recorded after the pure nitrogen exposure (typical for baked UHV systems), this spectrum exhibits a low ratio between the mass two peak and the rest of the signals. The high mass 18 signal should also be noted.

To check to what degree the performance of a baked UHV system is preserved by venting to pure nitrogen before opening the system, a 70 mm flange was dismantled during a nitrogen exposure. The nitrogen pressure in the system was held slightly above atmospheric pressure when removing the flange to avoid air from being sucked into the vacuum chamber.

As is seen in fig. 2, the desorption coefficients for all four desorbing species increased after this exposure as in the case of atmosphere exposure but the magnitude of the increase of the total desorption ($\eta_{CO} + \eta_{H_2} + \eta_{CH_4} + \eta_{CO_2}$) is nearly three times less. The increase in η_{H_2} and η_{CH_4} is, however, approximately the same in both cases. As is seen from the pumpdown curve (fig. 3, curve d) the evacuation rate is also considerably improved compared to the case of the air exposure. The mass spectrum recorded 23 hours after the exposure (fig. 4d) shows a strong mass 18 signal, typical of an unbaked system.

3.4 Effect of successive exposures to oxygen at low pressure

To investigate how the desorption coefficients change as a function of oxygen dose, a set of successive O_2 exposures to 1.10^{-5} torr for two hours, without intermediate bakeouts, were made, see fig. 5. The result for an O_2 exposure to one torr for two hours is presented in the same figure as comparison. The first exposure to oxygen at 1.10^{-5} torr led to a total desorption that was approximately 75% of the effect recorded after the 1 torr exposure (i.e. the dominant CO desorption was almost the same) while the η_{CO_2} after the first low pressure exposure was less than 50% of the η_{CO_2} after the exposure to one torr. The subsequent exposures to oxygen at 1.10^{-5} torr had a significant effect on the desorption of CO_2 and CH_4 while the total effect of all exposures on η_{H_2} was undetectable. The effect on η_{CO} seemed to have reached saturation after the first exposure.

After the five low pressure oxygen exposures, all of the same magnitude, the total desorption was $\approx 90\%$ of the value measured after the 1 torr exposure, while the CO_2 desorption was almost two times as high. It should be kept in mind that the exposure to 1 torr for one hour corresponds to a 10^4 times higher dose than the accumulated dose of the five low pressure exposures. The strong response in η_{CO_2} after the low pressure exposures could possibly stem from the fact that the filaments in the system (ion gauges etc.) were on during the low pressure exposure, see section 3.5.

After the desorption measurement following the third low pressure oxygen exposure, the system was left with pumps on for 250 hours, before a new desorption measurement was done. As is seen in the figure, the desorption of CO_2 and CH_4 decreased substantially, indicating that these species are comparatively weakly bound to the surface and are being pumped away. (Note that CO_2 is also the species that is strongest affected by the bakeout, see fig. 2).

3.5 Influence of hot filaments on the oxygen surface reactions

It is well known that excited oxygen molecules, formed at hot filaments, can strongly enhance the reaction rate for oxygen-surface reactions⁹⁾. It is also known that hydrogen will interact with hot filaments, leading to formation of atomic hydrogen that can form water by a reaction with surface oxides⁴⁾. It was shown in an earlier work that this water formation reaction, caused by hydrogen atomized at hot filaments, strongly affects the subsequent ion induced desorption³⁾.

To check if the ion induced desorption following an oxygen exposure is also affected if ion gauges etc. are left on during the exposure, two O_2 exposures at

1.10^{-5} torr for 2 h were made, one with and one without filaments on. As is seen from fig. 6, both exposures give an increase in η_{CO} , η_{CO_2} and η_{CH_4} while η_{H_2} exhibits a decrease. The relative magnitude of the increase in the desorption coefficients differ, however, significantly. With filaments on during the injection, the increase of η_{CO_2} is approximately two times higher than with filaments off, while the increase in η_{CO} after the exposure with filaments on is $\approx 50\%$ of the η_{CO} without filaments. These results can be explained if one assumes that the presence of excited oxygen, formed at hot filaments during the O_2 exposure, enhances CO_2 formation on the surface at the expense of CO formation.

4. Discussion and conclusions

That the vacuum performance of an UHV system is strongly related to what kind of atmospheres the chamber wall has been subjected to is an everyday experience for everyone working with ultrahigh vacuum technology. The most striking phenomenon is obviously the high degassing rate of water vapour in an unbaked system, although even this 'simple' fact is far from completely understood. As many authors have pointed out, the total amount of H_2O that desorbs during a vacuum bakeout can equal up to 100 monolayers^{10,11}) and it has become generally accepted that the water is bound throughout the oxide layer (passivation layer) of the stainless steel, probably as hydroxyl groups¹²).

The strong interaction between oxygen and the vacuum envelope is also well known and well exemplified by the problems encountered when injecting pure O_2 into a vacuum chamber. As is reported by Quinn and Elliot¹³), the residual gas composition after a dynamically stabilized injection of ultrapure oxygen to a pressure of 10^{-7} torr shows an impurity level of approximately 20% (mainly Ne, CO, H_2O and H_2).

These results are probably due both to an excessive pumping of oxygen by the chamber walls increasing the impurity to oxygen ratio (the high Ne contamination was explained in this way) and complex chemical reactions between the oxygen and the chamber wall and/or hot filaments.

In an earlier work it was shown by exposing the stainless steel surface to isotopic gases (D_2 , D_2O , $H_2^{18}O$ and $^{18}O_2$) that both oxygen and hydrogen atoms from the water and oxygen molecules were incorporated in the gases being desorbed (CO , H_2 , CH_4 and CO_2) during a subsequent ion bombardment³).

That the behaviour of the ion induced neutral gas desorption is strongly connected to the general behaviour of the vacuum system is clear and the reported results show that exposures to the two species that are by far the most

active in perturbing the surface conditions, i.e. H_2O and O_2 , give rise to distinctly different behaviour in both the ion induced desorption and the residual gas composition.

The main difference between the ion induced desorption after exposure to oxygen and water vapour, namely the decrease of hydrogen desorption after the oxygen exposure, is most simply explained by assuming that the oxygen reacts with hydrogen on the surface forming water. This assumption is also supported by the increase of the mass 18 signal in the residual gas spectra recorded after O_2 exposures. Comparing the influence on the total desorption yield after the air exposure with the effect recorded after injection of a pure nitrogen-oxygen mixture clearly shows that the effect of the water vapour dominates over the effect created by the oxygen when venting to normal air. It seems reasonable to assume that the influence of a normal air exposure is mainly a superposition of the effects created by the water vapour and the oxygen, with the effect of the water dominating. The effect of the oxygen interaction with the surface is also seen from the pumpdown curve after injection to the pure nitrogen-oxygen mixture. However, comparing this curve (fig. 3, curve c) with the one recorded after air exposure (fig. 3, curve b) clearly indicates, as one would expect, that it is the humidity in the air that is the big offender to the vacuum performance.

The surprisingly strong effect on the desorption of CO_2 that was seen after five consecutive low pressures ($1 \cdot 10^{-5}$ torr for 2 h each) exposures could be explained by the fact that those low pressure injections were made with hot filaments in the system, while these were obviously turned off during the injections to higher pressures. As was shown in a separate measurement, an oxygen exposure with the filaments on in the system seemed to change the ratio between CO_2 and CO desorption under subsequent ion bombardment, increasing the CO_2 desorption.

The influence of hot filaments is believed to be due to formation of excited oxygen which is known to have a drastic influence when making sticking coefficient measurements⁹⁾. The detailed chemical mechanism of the interaction is, however, not known.

The measurements of ion induced desorption, pumpdown time and residual gas composition after a nitrogen injection to atmospheric pressure with a flange removed for 45 minutes show that there is a significant decrease of the surface contamination compared to the situation after an air exposure. The effects recorded after the N_2 exposure with open system is, nevertheless, qualitatively similar to those seen after air exposure.

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FIGURE CAPTIONS

- Fig. 1 Schematic diagram of the experimental arrangement
(QMA = quadrupole mass analyzer, VG = vacuum gauge,
IP = ion pump, TSP = titanium sublimation pump,
TMP = turbomolecular pump).
- Fig. 2 The behaviour of the desorption coefficient η after exposures
to different atmospheres. The exposures were to atmospheric
pressure for one hour, except for O₂ (one torr for one hour)
and H₂O (1.10^{-5} torr for 2 hours) (B = Bakeout).
- Fig. 3 Pumpdown curves for the first 40 minutes of the evacuation
after the atmospheric pressure exposures.
- a : exposure to nitrogen, b : exposure to normal air
 c : exposure to an 80% nitrogen, 20% oxygen mixture
 d : exposure to nitrogen with a 70 mm flange removed for 45
 minutes
- Fig. 4 Residual gas spectra recorded 23 hours after initialization
of pumpdown from atmospheric pressure. The total pressure
when recording the spectrum is given in each case.
- a : after N₂ exposure
 b : after air exposure
 c : after exposure to 80% N₂, 20% O₂
 d : after N₂ exposure with a 70 mm flange removed for 45
 minutes
- Fig. 5 Behaviour of the desorption coefficients η after oxygen
exposures. Exposure 1 corresponds to 1 torr for 1 hour,
while exposures 2-6 correspond to 1.10^{-5} torr for 2 hours
each (B = Bakeout).
- Fig. 6 Behaviour of the desorption coefficients η after exposure to
O₂ (1.10^{-5} torr for 2 hours) with and without filaments
heated during exposure (B = Bakeout).

FIG.1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6