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ION INDUCED DESORPTION FROM STAINLESS STEEL STUDIED WITH ISOTOPE TECHNIQUES*

by

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ABSTRACT

The change in the ion stimulated desorption of neutral gas from vacuum baked stainless steel 304 L at room temperature due to preceding exposures to different gases (1.10^{-5} torr for 2 h) has been studied. The gas species desorbing during Ar^+ bombardment (ion current density $\approx 1.10^{-8}$ A/cm², ion energy ≈ 520 eV) were: CO, H₂, CH₄ and CO₂.

The strongest influence on the desorption was caused by exposures to H₂O and O₂. Exposure to H₂ also affected the desorption but this is shown to be a consequence of H₂O production resulting from a reaction between atomic hydrogen formed at hot filaments and the oxide layer of the stainless steel.

Exposures to CO, CO₂, CH₄, Ar and N₂ had a small or undetectable influence on the desorption.

Exposures to the isotopic species O₂¹⁸, D₂O, D₂ and H₂O¹⁸ showed that isotopic exchange between the absorbing and desorbing gas took place in all four cases. A model is proposed that explains the observed isotopic exchange in terms of chemical reactions catalysed by the metal oxide (passivation layer) on the stainless steel.

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1. INTRODUCTION

The phenomenon of ion induced neutral gas desorption has to be carefully taken into account when designing ultrahigh vacuum systems where the vacuum chamber wall is exposed to fluxes of energetic ions, as in proton storage rings and fusion devices¹⁻⁵). At the Intersecting Storage Ring (ISR) facility at CERN, Geneva, the maximum circulating beam current may be limited by vacuum instabilities caused by desorption of strongly bound surface gas, not previously removed by the standard 24 h, 300°C bakeout. This desorption occurs when residual gas molecules are ionized by the proton beam and accelerated into the wall by the space charge of the protons (approximately 2 kV at a beam current of 30 A).

The ion induced desorption from technological vacuum chamber materials such as stainless steel, inconel, aluminium and titanium has been extensively studied during the last decade⁶⁻¹⁶), and as a result of improved cleaning techniques (chemical solvent cleaning, vacuum annealing, glow discharge cleaning) the vacuum limited stored current in the ISR is now approximately four times the value achieved seven years ago. Those investigations have, however, revealed that the mechanism of ion induced desorption is complex, and the results suggest that the chemical activity of the near surface region of the vacuum chamber material has to be taken into account to get a good understanding of the process^{15,16}).

The desorption efficiency is conveniently quoted in terms of η_x values, defined as the number of desorbed molecules of gas species x per impinging ion. In the case of the real storage ring with a residual gas containing H_2 , CH_4 , CO and CO_2 one has to take into account that the ion flux consists of more than one species, and furthermore, that the ratio between these different bombarding species will change as the residual gas composition changes. In the laboratory, however, the measurement is normally designed in a way that limits the bombarding ion flux to one type of ion, normally a rare gas ion such as Ar^+ . The values increase as a function of ion energy for energies up to (at least) 3 keV⁷) and for a given energy a heavier ion gives a higher desorption¹²). Typical η values for the four gases normally desorbing from a stainless steel surface due to ion impact, i.e. CO , H_2 , CH_4 and CO_2 , are summarized in Table 1 as a function of different pretreatments. As is seen from the table, the gas released during ion bombardment is predominantly CO and H_2 and, as is shown in ref. 10, the amount of CO desorbing during a glow discharge corresponds to many tens of monolayers. This is a surprisingly high value. It should also be emphasized (see Table 1) that the glow discharge treatment leaves the surface in a state that gives reduced desorption values even after a long re-exposure to the atmosphere.

The purpose of this work was to study how chemical reactions taking place on the surface of stainless steel 304 L affected the ion stimulated desorption. For this investigation, the surface was exposed to isotopically marked gases (O_2^{18} , D_2 , D_2O , H_2O^{18}), followed by measurements of the changes in the gas composition due to ion bombardment.

2. EXPERIMENTAL

2.1 Vacuum system

The layout of the experimental apparatus is shown in Fig. 1, see also ref. 11. The vacuum system consisted of a 5 m long tube, 5 cm in diameter, made of the material under study, in this case stainless steel 304 L. At each end a pump station was mounted, each one comprising an 80 l/s sputter ion pump and a 1000 l/s titanium sublimation pump. At one end the system was equipped with a 100 l/s turbomolecular pump, backed by a rotary pump. At the centre of the tube a quadrupole mass spectrometer (Balzers QMG 511) was fitted. The gauge positions are indicated in the figure. The complete system was bakeable to 300°C. The ultimate pressure was approximately $2 \cdot 10^{-11}$ torr as measured at the ends of the tube. A 1 mm thick titanium wire was strung along the tube axis and connected to the outside through electrical feedthroughs. A small thoriated tungsten filament was mounted at the centre of the tube to serve as the electron source required for the desorption measurements.

The electrical connection of the central Ti-wire and the filament permitting one to measure the electron emission current and the resultant ion current bombarding the wall, is indicated in the figure.

2.2 Desorption measurements

During a measurement the chamber was filled to $9 \cdot 10^{-6}$ torr of argon. When the electron source is on and a positive voltage (+ 520 V) applied to the wire, the emitted electrons are trapped in closed orbits around the central wire (orbitron configuration) and drift along the tube causing ionization of the argon in the tube. These positive ions are repelled by the positive wire, and cause desorption when impinging on the tube wall. To minimize the pressure decrease of argon due to implantation in the wall, the argon was kept flowing during the measurement. With this method a pressure equilibrium was obtained during the ion bombardment lying approximately 5% lower than that when no ions were being implanted.

During ion induced desorption with ions originating from ionization of gas at constant pressure (no positive feedback), the following continuity equation gives the pressure profile along the tube¹⁷⁾:

$$qU + \frac{i\eta U}{\gamma e} + C \frac{d^2 P(x)}{dx^2} = 0 \quad (1)$$

where P pressure (torr)

q specific outgassing (torr cm/s)

i ion current density (A/cm²)

η desorption efficiency (number of molecules desorbed per incident ion)

e elementary charge (As)

γ conversion factor from molecules to torr cm³

U perimeter (cm)

C conductance per unit length (cm⁴/s).

Boundary conditions : at x=0, $\frac{dP}{dx} = 0$ by symmetry

$$\text{at } x = \pm L/2, \quad SP = \frac{LU}{2} \left(q + \frac{i\eta}{e\gamma} \right)$$

where L/2 is tube half-length (cm) and S the pumping speed (cm³sec⁻¹) at each end.

The solution of (1) with these boundary conditions is :

$$P(x) = U \left[\frac{i\eta}{e\gamma} + q \right] \left[\frac{L}{2S} + \frac{L^2}{8C} - \frac{x^2}{2C} \right]$$

Pressure at x = 0 when 4C/LS << 1 (conductance limitation) :

$$\text{no desorption : } P_0 = qU \frac{L^2}{8C}$$

$$\text{desorption : } P_1 = U \left(\frac{i\eta}{e\gamma} + q \right) \frac{L^2}{8C}$$

$$\Delta P = P_1 - P_0 = \frac{U i \eta L^2}{e \gamma 8 C}, \quad \eta = \frac{\Delta P e \gamma 8 C}{U i L^2}$$

Thus, if the conductance of the tube was known and the pumping speed at the ends high in relation to the conductance, the η_x could be determined by a measurement of the partial pressure increase ΔP_x for a known ion current density. The electron induced desorption caused by the electrons hitting the central wire was negligible compared with the ion induced desorption for CO, CH₄ and CO₂. For H₂, however, the electron desorption contributed approximately 20% to the pressure rise which had to be taken into account when calculating the η values.

In order to deduce the partial pressure for CH₄ (mass 16) from the mass spectra, it had to be taken into account that CO in its cracking pattern has a peak at mass 16 (O⁺), being = 1% of the main peak. The assumption that the system was conductance limited was clearly justified for H₂, CO and CO₂, as those gases were efficiently pumped by the sublimation pumps, having a nominal pumping speed of 1000 l/s, while the conductance along the tube, C/L, equals 3.1 l/s for mass 28. For mass 16 (CH₄), however, this did not hold, as the pumping speed for this gas is very low for a sublimation pump. The pumping speed for CH₄ was thus provided mainly by the 100 l/s turbomolecular pump used to keep the argon flowing. Thus, to calculate the desorption coefficients for CH₄, eq. (1) had to be solved with boundary conditions corresponding to the unsymmetric situation with pumping only at one end of the tube. The assumption of conductance limitation was made for this case too, leading to an error of less than 15%.

To minimize the errors due to long term instability of the quadrupole electron multiplier sensitivity, the gas analyzer was always calibrated before a measurement against the argon pressure as read on the ion gauge positioned in the middle of the tube.

To study how different gas exposures affected the η values the following measurement cycle was adopted :

1. The complete vacuum system was baked to 275°C for more than eight hours to reset the initial state of the surface. This treatment was effective in bringing down the η values after the gas exposures. After many bakeout cycles, these 'base η values' tended to decrease, indicating that a slow cleaning of the surface was taking place. The η values were measured at room temperature (' η after bake', marked B in the figures).
2. The desired gas was injected into the vacuum chamber via an all metal UHV injection system (except for water vapour). All exposures were $1 \cdot 10^{-5}$ torr, as read on the centrally placed gauge, for two hours. The non-isotopic gases used were high purity (better than 99.99 %) gases supplied by Carbagas. To inject water vapour into the system, demineralized water was frozen by immersing a test tube, attached to the gas inlet system, into liquid nitrogen. The gas over the

ice was then pumped away with the turbomolecular pump before the ice was melted. During all the exposures the gas composition was monitored with the mass spectrometer.

3. After having pumped the system to a pressure of less than $2 \cdot 10^{-9}$ torr (except after the atmospheric exposure when the pressure was still $5 \cdot 10^{-8}$ torr) the η values were measured to give the ' η after exposure' values. The time required to reach this pressure was strongly dependent on the injected gas and varied between 7 minutes (for N_2) and ≈ 24 h (for H_2O).

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 $150^\circ C$. The subsequent vacuum anneal is done in an industrial vacuum furnace for 2 hours at $950^\circ C$ and at a pressure of less than $1 \cdot 10^{-5}$ 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 CO_2 , CO , H_2 , H_2O , O_2 , CH_4 , N_2 , and atmosphere

Fig. 2 shows the variations of η_{CO} , η_{H_2} , η_{CH_4} and η_{CO_2} when the tube was subjected to the indicated series of gas exposures and bakeouts. As the system had to be opened once during the measurement series, one point corresponds to an atmosphere exposure lasting 2 h 45 min. The four species indicated in the figure, CO , H_2 , CH_4 and CO_2 are the only detectable gases desorbing from a baked stainless steel surface during ion impact under normal conditions. An argon exposure was done as a check of the cleanliness of the injection technique as a rare gas is not expected to influence the desorption because of its lack of chemical activity. The difference in the η values as measured before and after the argon exposure can thus be taken as a measure of the reproducibility of the measurements. The strongest influence on the desorption was seen after exposures to O_2 and H_2O (disregarding the effect of the atmosphere exposure). As is seen in the figure, the oxygen injection gave increases in η_{28} and η_{44} while the water exposure gave a response in all four η values. A small decrease in η_{H_2} is always seen after O_2 exposures. The increase in desorption yield after hydrogen exposure is a consequence of H_2O formation in the vicinity of hot filaments, see paragraph 3.4. The exposures to CO and CO_2 had a surprisingly small influence on the η values, while the H_2 exposure gave a response

in both η_{CH_4} and η_{CO_2} . The effect of this H_2 injection on η_{CO} and η_{H_2} is not considered as significant, but after a H_2 injection made at a later stage in the measurement series, an effect is seen for these species as well (see figs. 5 and 7). The progressive cleaning of the tube is believed to account for this increase in sensitivity to H_2 exposure. The N_2 exposure did not affect the desorption significantly, while the CH_4 exposure had a small influence on η_{CH_4} and η_{CO_2} .

3.2 Exposure to O_2^{18} and O_2^{16}

In order to investigate the chemical activity of the surface, a series of desorption measurements were done after exposures to isotope marked gases. This method gave the possibility to determine unambiguously whether the desorbed molecule contained a marked atom originating from the previously injected gas and could thus yield valuable information about how chemical reactions on the surface influenced the desorption.

Fig. 3 shows the effect on the η values when exposing the tube to O_2^{16} and O_2^{18} . In the right hand column, the η values for different masses corresponding to similar types of molecules have been added together to facilitate a comparison with the effect of the O_2^{16} exposure. As is seen in the figure, the O_2^{18} exposure gave rise to three new desorbing masses, 30 (CO^{18}), 46 ($CO^{16}O^{18}$) and 48 (CO_2^{18}). For CO, the increase in desorption seemed to be entirely due to CO^{18} (mass 30) desorption. In the case of CO_2 , however, the increase was due to increases of the η values for all three corresponding masses, namely CO_2^{16} (44), $CO^{16}O^{18}$ (46) and CO_2^{18} (48). Note that $\eta_{CO_2^{16}}$ increases after exposure to O_2^{18} , even though the two molecules have no atoms in common. The subsequent bakeout did not bring down the desorption of the O_2^{18} containing molecules, nor the corresponding peaks in the residual gas spectrum, to the zero level.

3.3 Exposure to D_2O^{16} , H_2O^{18} and H_2O^{16}

Fig. 4 shows the effects of exposures to D_2O^{16} , H_2O^{18} and H_2O^{16} . After the H_2O^{16} and H_2O^{18} exposures the increase in hydrogen desorption was mainly due to mass 2 while after the D_2O^{16} exposure it was the increase in the masses 3 (DH) and 4 (D_2) that dominated. It should be emphasized that η_{DH} was higher than η_{D_2} after the D_2O^{16} exposure. After the D_2O^{16} exposure, the masses 17 and 18 were desorbing. Those new peaks in the desorption spectrum were assigned to CH_3D (17) and CH_2D_2 (18). Mass 18 is not believed to correspond to water desorption, as this mass was not desorbed after H_2O^{16} exposure. (Desorption of the masses 19 and 20, corresponding to the isotopes CHD_3 and CD_4 , could not be monitored because of interference with the strong mass 20 peak from argon).

The masses 3, 17 and 18 could still be desorbed after bakeout, and were to some extent influenced by the H_2O^{16} and H_2O^{18} exposures. The desorption of mass 16 corresponding to CH_4 , increased after all three exposures, which in the case of D_2O^{16} exposure is surprising because of the lack of common atoms in the desorbed molecule and the injected gas. The contribution from mass 30 to the increase in CO desorption was strongest in the case of H_2O^{18} exposure, as would be expected. The CO_2 desorption was composed of all three masses, 44, 46 and 48, except after the H_2O^{16} exposure where no 48 signal was recorded.

After the H_2O^{18} exposure the contribution to the CO_2 desorption increase was still dominated by the mass 44 (CO_2^{16}). (Compare with the mass 44 increase after O_2^{18} exposure).

3.4 Exposure to H_2 and D_2

In Fig. 5, the effect of a D_2 exposure is compared with that from ordinary hydrogen. The hydrogen and deuterium exposures affected the desorption of all four molecules (CO , H_2 , CH_4 and CO_2), and were in that respect similar to the water exposure, even though the increases were lower in the case of hydrogen.

The mass spectra recorded during H_2 and D_2 exposures showed that water was formed in the system. Fig. 6 shows a mass spectrum recorded during the D_2 exposure where the peaks 20 and 22 correspond to D_2O^{16} (20) and D_2O^{18} (22). The D_2O^{18} corresponds to water formed by a reaction between the deuterium and the O^{18} still remaining on the surface after the exposure to isotopic oxygen. The water formation reaction on stainless steel is reported elsewhere in the literature^{15, 16, 18}) and is strongly enhanced if the steel is exposed to atomic hydrogen that is normally formed at any hot filaments during the hydrogen exposure^{15, 16}). In order to check if the increase in desorption yield after the hydrogen and deuterium exposures was due to water formed as a result of a reaction between atomic hydrogen formed at hot filaments and the oxide layer of the stainless steel, a hydrogen exposure was done with all filaments in the vacuum system turned off. During this measurement the pressure was monitored with a Penning gauge in a pumped side-arm of the system.

In fig. 7 the changes in η -values after H_2 exposure with and without filaments on are compared. The lack of response in desorption yield after the H_2 exposure without hot filaments clearly shows that the effect on the η values after the hydrogen exposures shown in figs. 2, 5 and 7a is entirely due to the water formed near these filaments and not to the hydrogen itself. The strongly enhanced water peak in the residual gas spectrum that was recorded after the H_2 exposures with filaments on was also absent when the H_2 exposure was made with filaments off.

4. DISCUSSION

In order to understand the response in desorption after gas exposures, attention has to be focussed on the surface oxide layer (passivation layer) of the bulk material, stainless steel 304 L. The composition and structure of the surface of stainless steels have, as a consequence of their great commercial importance, been extensively investigated, mainly within the field of corrosion science¹⁹⁻²⁷). The composition of the oxide layer is sensitive to the conditions under which it is formed (oxidising medium, temperature, time, etc.) as well as to the composition of the alloy^{22, 23, 27}). Typical thickness of an oxide layer formed in air at room temperature is 50-100 Å. There is strong evidence that the oxide layers on steels of similar type as that studied in this work exhibit a layered structure. If oxidised at room temperature in air or oxygen, depth profile measurements have shown that the topmost layer of the oxide is enriched in iron oxide^{21, 22, 23, 28}). There is also evidence for a thin chromium oxide enriched layer at the metal-oxide interface which is believed to account for the passive properties of the steel^{21, 22, 23, 28}). When stainless steel is oxidised in a water containing atmosphere, water will be trapped in the oxide layer (hydration), either in the form of water molecules or as OH groups^{19,20,26,27}). The amount of bound water in a passive oxide film on Fe, measured with a radiotracer technique, is given as two H₂O molecules per Fe₂O₃ molecule²⁹), while the amount of water in hydrated bulk chromium oxide is quoted as an H₂O/Cr₃+ ratio of 2.3-2.5³⁰). The water bound in the oxide layer can thus very well correspond to several tens of monolayers, a value that corresponds well to the amount of water that desorbs from a stainless steel vacuum envelope during bakeout³¹).

Another interesting aspect of the passivation layer is in its catalytic property, as it is well known that the oxides of Cr, Fe and Ni exhibit catalytic activity^{32,33}). In order to activate these oxides, they are normally heated in vacuum or an inert atmosphere to a temperature of 400-500°C. Burwell et al.³⁰) have, for the case of chromium oxide, proposed that the active sites that develop during heat treatment in vacuum are "coordinatively unsaturated surface ions" formed by loss of water. The oxide covered and baked stainless steel vacuum envelope can thus be expected to show chemical activity.

To account for the present results, the following model is proposed that postulates a chemically active oxide layer that provides binding states for oxygen molecules that will make them more easily available for chemical reactions than those incorporated in the oxide. Fig. 8 is a schematic picture of the surface layer after different treatments corresponding to the different steps of the performed experiment. The occurrence of carbon on the surface of solvent cleaned and baked stainless steel is well established by Auger measure-

ments, but the chemical state of the carbon is obscure. Chemical shifts in the Auger peak from carbon indicates however that the carbon exists in the form of carbides within the oxide layer^{6,21,22,23}). Fig. 8b represents the dehydration and catalytic activation during bakeout. When exposing to oxygen, the oxygen molecules are trapped on active sites providing binding states that will allow the oxygen molecules to take part in reactions to form CO and CO₂ (Fig. 8c). It is necessary to assume that the oxygen from the exposure differs from the oxygen incorporated in the oxide with respect to its availability for chemical reactions, otherwise it is hard to account for the strong increase in desorption when exposing to oxygen, as this species is abundant in the oxide before the exposure. The water vapour exposure is doing the opposite to the bakeout, that is it hydrates the surface (Fig. 8d). If the H₂O is dissociated into H and OH groups, and the oxygen in the OH groups is more reactive than the oxide oxygen, this can explain the formation of all four molecules seen to increase their desorption. The possibility should not be excluded that the reactions during oxygen exposure also involves formation of H₂O as an intermediate product. The proposed reactions are given in the figure.

As shown experimentally in section 3.4, the desorption increase due to hydrogen exposure is entirely due to water formed when atomic hydrogen, produced at hot filaments, impinge on the vacuum chamber wall. Water is formed as a result of a reaction between atomized hydrogen and oxide oxygen and this water dissociates as described above. This corresponds to a transfer of oxygen atoms to a less strongly bound state. The effects of the hydrogen exposure can thus be described with a similar reaction scheme as that proposed for the water exposure.

To what extent the energy transfer to the oxide layer during the bombardment with argon ions (energy ≤ 520 eV) triggers the reaction between the surface carbon and the reactive oxygen from the O₂ or H₂O exposures is an open question.

The strong increase in the CO₂ and CO signals in the residual gas spectrum after O₂ exposure does however suggest that these molecules are already, at least partially, formed during the exposure phase and not only during the ion bombardment. Similarly, after H₂O exposure, an increase is seen for the peaks in the residual gas spectrum corresponding to H₂, CH₄, CO and CO₂, i.e. the same species as these increasing their desorption yield when subsequently bombarding with argon ions. The anomalies in the desorption response of CO₂¹⁶ after exposure to O₂¹⁸ and H₂O¹⁸ as well as the increase in desorption of CH₄ after exposure to D₂ and D₂O cannot be explained directly by the reaction scheme given above. In those cases an increase in desorption yield is observed for a mole-

cule that has no atoms in common with the exposing gas. If, however, an exchange reaction takes place, substituting a fraction of the adsorbed oxygen with oxide-bound oxygen, this could explain the response in $\eta_{CO_2}^{16}$ after exposure to O_2^{18} . Reactions of this kind, involving exchange between adsorbed and oxide-bound oxygen on both Cr_2O_3 and Fe_2O_3 are reported in the literature³³). This is also consistent with the observation that the marked oxygen remains on the surface after many bakeout cycles and can be incorporated in water molecules during subsequent exposures to H_2 and D_2 (see fig. 6).

A more complex mechanism responsible for the desorption response in those cases can, however, not be ruled out.

5. APPLICATIONS TO THE ISR

The measurements reported here strongly suggest that the properties of the oxide layer are dominant in determining the ion induced desorption behaviour of stainless steel. A natural continuation would be to investigate whether those properties can be altered in a way that :

- (a) decreases the ion induced desorption from the walls of the vacuum chamber, and
- (b) can be applied to a large scale system as the ISR in a way that is economically and practically feasible.

The last criterion probably excludes in situ treatments as such methods would turn out too costly to apply to a machine not specifically designed for it. This implies that the treatment in question must be stable to atmosphere exposure so that an air exposed vacuum chamber surface after pumpdown and bake-out exhibits a lower desorption yield. (The glow discharge cleaning as done at ISR is, to a certain extent, an example of such a treatment, see table 1). Two ways to influence the stainless steel surface will be considered.

1. to change the distribution of the different oxide species within the oxide layer.
2. To cover the clean metal surface with an inert material (such as gold) to prevent the oxide from being formed when exposed to an oxidising atmosphere.

As was mentioned in paragraph 4, there exists strong evidence that the oxide layer on stainless steel formed in air at room temperature has a layered structure with iron oxide at the top and chromium oxide at the metal-oxide interface^{21, 22, 23, 24}). This layered structure can, however, be influenced by changing the oxidation parameters. For example, in order to improve the corrosion resistance it is desirable to obtain a surface film enriched in chromium oxide at the oxide-gas interface³⁴). Surman et al. report that this surface

structure can be achieved for a 9% Cr, 1% Mo steel either by a high temperature (580°C) pre-oxidation in air or a selective pre-oxidation in a H_2/H_2O mixture at a temperature exceeding 440°C.

L.C. Beavis¹⁸⁾ noticed that the water production at a stainless steel 304 surface during hydrogen exposure at elevated temperature was inhibited if the surface was previously exposed to 10^{-5} torr of O_2 at 900°C. This effect was attributed to the formation of a Cr_2O_3 layer at the oxide-gas interface that was less active than the normal iron oxide with respect to the water formation reaction.

These data suggest that the Cr_2O_3 enriched surface is less chemically active than the 'normal' (iron-oxide rich) surface, and it would therefore be of interest to investigate whether the chemical reactions leading to increased ion induced desorption can be suppressed by changing the oxide structure. Such a surface would then be 'non-contaminatable' by atmospheric exposure and thus remove the necessity of in-situ preparation.

Measurements are now in progress to clarify whether this approach can lead to permanent reduction of the ion induced desorption in practical cases. These measurements will proceed in two steps:

- (a) depth profiling of oxidised stainless steel samples by means of Auger spectroscopy combined with ion etching in order to establish the optimal oxidation parameters to achieve the desired Cr_2O_3 rich oxide layer.
- (b) measurements of the ion induced desorption yield and the sensitivity of the n-values to gas exposures for a pre-oxidised surface.

In conjunction with these measurements, it is planned to investigate, on exposure to the atmosphere, the behaviour of an oxide free stainless steel surface which is protected from direct re-oxidation by a thin in-situ evaporated gold layer.

6. CONCLUSIONS

The increase in ion induced desorption from stainless steel after gas exposures has been shown to be governed by a more complex mechanism than a simple adsorption-desorption process where the molecules of the exposing species maintain their identity.

By far the strongest effect on the desorption yield is seen after exposures to oxygen or water vapour. Whereas the water exposure affects the desorption of all four gas species that normally desorb from a stainless steel envelope on ion bombardment, i.e. CO, H_2 , CH_4 and CO_2 , the oxygen exposure increases only the desorption of CO and CO_2 .

By exposure to isotopically marked gases it has been shown that the adsorption-desorption mechanism frequently involves dissociation of the adsorbed molecule and the subsequent incorporation of the fragments in the desorbed molecule.

Exposure to hydrogen leads indirectly to the formation of water as a result of a reaction between the oxide layer and atomic hydrogen created at hot filaments (see refs. 15 and 16). The water formed in this way will influence the ion induced desorption while it has been shown that a hydrogen exposure without hot filaments in the vacuum system does not have a detectable influence on the desorption yield.

The chemical activity of the oxide layer, enhanced by the dehydration during bakeout, is believed to account for the main features of the reported results.

That the desorbed species mainly originate from the oxide layers is also in agreement with the results obtained for glow discharged stainless steel (refs. 7 and 8). The in-situ glow discharge treatment leaves behind an oxide free alloy surface, as seen by Auger spectroscopy, and gives a desorption yield far below that from an oxide covered surface (see Table I).

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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 gases. All exposures except that marked ATM were 1.10^{-5} torr for 2 hours. The exposure marked ATM corresponds to air of atmospheric pressure for 2 h 45 min. (B = Bakeout).
- Fig. 3 Behaviour of the desorption coefficient η after exposures to O_2^{16} and O_2^{18} (1.10^{-5} torr for 2 h). Column c corresponds to the same exposure (O_2^{18}) as column b, but with the desorption coefficients for the indicated masses added together. The triangles indicate desorption coefficients for masses that did not desorb before the indicated exposure.
- Fig. 4 Behaviour of the desorption coefficient η after exposures to D_2O^{16} , H_2O^{18} and H_2O^{16} (1.10^{-5} torr for 2 h). Columns b, d and f correspond to the same exposures as in columns a, c and e, but with the desorption coefficients for the indicated gases added together. The triangles indicate desorption coefficients for masses that did not desorb before the indicated exposure.
- Fig. 5 Behaviour of the desorption coefficient η after exposures to H_2 and D_2 (1.10^{-5} torr for 2 h). Columns b and d correspond to the same exposures as columns a and c but with the desorption coefficients for the indicated masses added together. The triangles indicate desorption coefficients for masses that did not desorb before the indicated exposure.
- Fig. 6 Mass spectrum recorded during exposure to D_2 . The mass peaks 20 and 22 indicates the formation of the molecules D_2O^{16} and D_2O^{18} . The O^{18} is evidently present in the oxide layer since an earlier exposure to O_2^{18} .
- Fig. 7 Behaviour of the desorption coefficient η after exposure to H_2 (1.10^{-5} torr for 2 h) with and without filaments heated during exposure.
- Fig. 8 Schematic picture of the oxide layer after different treatments, corresponding to the performed experiments (the lines between atoms do not represent bonds in a strict chemical sense). The asterisk on the oxygen atoms in Fig. 7c indicates that those atoms, originating from the exposing gas, are bound in weaker binding states than the oxygen atoms incorporated in the oxide. See paragraph 4.

TABLE 1

Typical η values for stainless steel after different treatments

These η measurements were done with $^{15}\text{N}_2^+$ ions with an energy of 2 keV. All data from reference 7.

SC = ISR solvent cleaning, B = 300°C bake for 24 h,

GD = Ar glow discharge, $8.5 \cdot 10^{17}$ ions/cm².

Treatment	η_{CO}	η_{H_2}	η_{CH_4}	η_{CO_2}
SC	10	10	0.5	1.5
SC + B	2	1.8	0.09	0.03
SC + B + GD *	< 0.01	< 0.01	< 0.01	< 0.01
SC + B + GD + atm. exposure for 12 h followed by pumpdown and 300°C bake.	0.95	0.35	0.02	0.01

* After this treatment argon was desorbing with $\eta_{\text{Ar}} = 0.08$.

69358

FIG. 1

FIG.2

FIG. 3

FIG. 4

69356

FIG. 5

60362

FIG. 6

69361

FIG. 7

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FIG. 8