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Electron Stimulated Molecular Desorption of a NEG St 707 at Room Temperature

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Electron stimulated molecular desorption (ESD) from a NEG St 707[®] (SAES Getters[™]) sample after conditioning and after saturation with isotopic carbon monoxide^{2, 13}C¹⁸O, has been studied on a laboratory setup. Measurements were performed using an electron beam of 300 eV kinetic energy, with an average electron intensity of $1.6 \cdot 10^{15}$ electrons s⁻¹. The electrons were impinging on the 15 cm² target surface at perpendicular incidence. It is found that the desorption yields η (molecules/electron) of the characteristic gases in an UHV system (hydrogen, methane, water, carbon monoxide, carbon dioxide) for a fully activated NEG as well as for a NEG fully saturated with ¹³C¹⁸O are lower than for OFHC copper baked at 120 °C. A small fraction only of the gas which is required to saturate the getter surface can be re-desorbed and thus appears to be accessible to ESD.

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Abstract

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Key words: Getter, Non Evaporable Getter, Desorption, Electrodesorption

1 Introduction

Non evaporable getters (NEG) have been used with great success in the LEP machine at CERN for over 10 years and have been instrumental in achieving and maintaining low pressures in a low conductance vacuum system typical for many high energy particle accelerators. In spite of the outstanding success of the linearly distributed NEG pump in the LEP e⁺e⁻ storage ring, surprisingly little work has been done to study photon or electron stimulated molecular desorption from such getter surfaces and its dependence on the surface saturation with adsorbed gas molecules.

For the next generation accelerator at CERN, the Large Hadron Collider

² cf nomenclature in [1]

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(LHC), it is planned to make extensive use of getter pumping. Even though most of the LHC vacuum system (approx. 23 km) will be at cryogenic temperature and therefore will depend on cryo-pumping by the cold beam pipe, the remaining 4 km at room temperature constitute a real challenge to the vacuum engineer. To obtain more complete data and a better understanding of the performance of a getter surface under realistic accelerator conditions, a test program has been started at CERN [2]. In this paper the results on ESD will be reported.

For practical reasons the commercially available and widely used NEG St 707[®] CTAM/30D (Zr 70%, V 24.6%, Fe 5.4%) [3] [4] ribbons from SAES GettersTM have been used. The kinetic energy of 300 eV of the electrons has been chosen in view of the estimated average energy of photo electrons produced in the vacuum chamber of the LHC and the corresponding large secondary electron yield of different technical surfaces shown in [2].

In order to be able to distinguish between ESD of molecules diffusing from the bulk and molecules accumulating on the surface by a controlled saturation, an isotopic carbon monoxide has been used. Indeed, saturating the surface with ¹³C¹⁸O instead of “conventional” CO, should allow a differentiation between the molecules deposited on the surface and pre-existing CO coming from the bulk. Furthermore, the isotopic CO could be used as a tool to find out whether CO molecules dissociate [5] [6] on the surface and recombine with other atomic species present on the surface before being desorbed. Unfortunately the gas which was available for these measurements was of insufficient purity since it contained significant ad-mixtures of “normal” C and O.

2 ESD Experimental Setup

The experimental set-up for ESD studies consists of two all-metal vacuum chambers, a pumping chamber and a test chamber as represented in Figure 1. The two chambers are separated by a known conductance C ($C_{28} = 55.3$ l/s at 300K) [2]. The system is bakeable and is evacuated by a turbomolecular pump.

The test chamber is equipped with a calibrated Bayard Alpert gauge (type SVT 305) and a quadrupole mass analyser (RGA, Balzers QMG 125). The electrons are produced by a hot filament and are accelerated toward the target by applying a positive bias voltage on the target. The sample manipulator contains two sample holders placed at 90 degree from each other. Each sample holder is equipped with a K type thermocouple, a polarisation wire for the bias voltage and can be heated by its own PBN³ oven. The targets are attached

³ PBN : Pyrolytic Boron Nitride

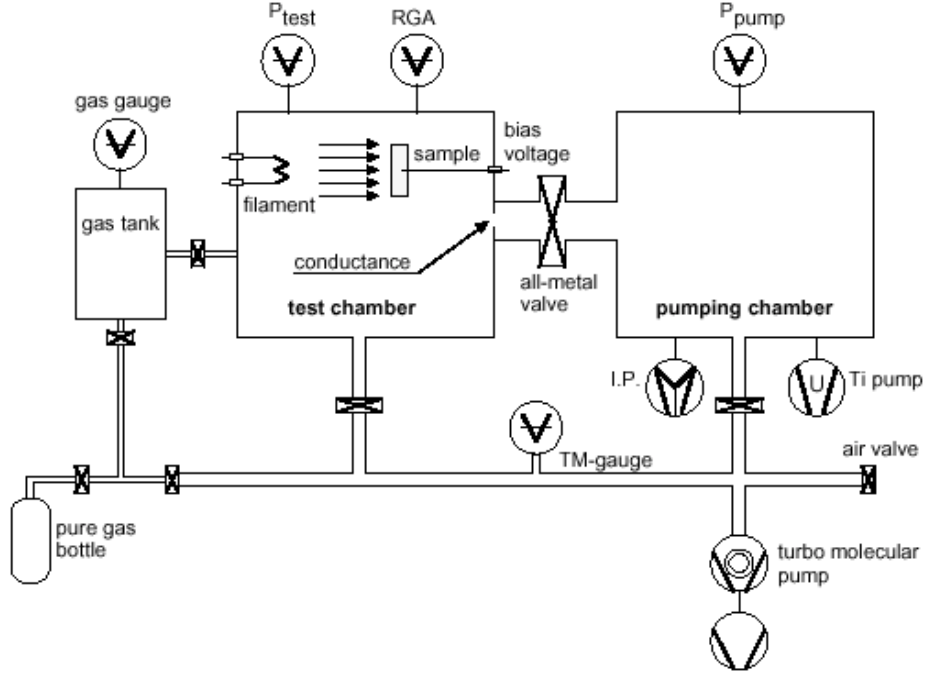


Figure 1. ESD experimental setup

by screws onto the sample holders. The targets for the ESD measurements are made of OFHC copper and NEG St 707.

The pumping chamber is equipped with an ion pump (IP) of 400 l/s nominal pumping speed for nitrogen and a titanium sublimator (TiSP), which can be cooled with liquid nitrogen, with a pumping speed of ~ 1100 l/s nominal pumping speed for hydrogen. The total pressure in the pumping chamber is measured with a calibrated Bayard-Alpert gauge (type SVT 305).

3 Molecular Desorption

The determination of the ESD yield η and the method used to calculate the total number of molecules which are desorbed during the irradiation have been described in [2].

The expression of the ESD yield is given by Equation (1). The flux of gas desorbed during the irradiation is measured by the pressure drop on both sides of the calibrated conductance, Figure 1. Using the definition of the ESD coefficient η and by satisfying the condition that the pressure in the pumping

chamber is much lower than in the test chamber one obtains the equation :

$$\eta \approx G \frac{C \Delta P_{NEG}}{\dot{\Gamma}} \quad (1)$$

Where :

$\dot{\Gamma}$ is the number of electrons impinging on the target per second.

C is the conductance in l s^{-1} for each gas species.

ΔP_{NEG} is the partial pressure increase in the test chamber under electron irradiation.

G is a constant, converting gas quantities (Torr l) to number of molecules ($\sim 3.2 \cdot 10^{19}$ at 300 K).

When the NEG is activated, it is no longer permitted to apply this simple expression since in this case the additional pumping of the NEG must be taken into account. It is therefore necessary to correct Equation (1) by the additional NEG pumping speed S_{NEG} (l/s), hence one finds :

$$\eta \approx G \frac{(C + S_{NEG}) \Delta P_{NEG}}{\dot{\Gamma}} \quad (2)$$

The total number of molecules desorbed during the irradiation is obtain by integrating the partial pressures with respect to time :

$$N_T = \int_0^{t_{off}} \eta \dot{\Gamma} dt = \int_0^{t_{off}} G C \Delta P_{NEG} dt \quad (3)$$

between the beginning of the irradiation and t_{off} , the time at the end of the experiment.

In the experimental system the presence of hot filaments may induce thermal gas desorption from the surrounding surfaces. The measured outgassing flux of 10^{-9} Torr l s^{-1} for hydrogen leads to a lower limit for the measurement of η of $2 \cdot 10^{-5}$ hydrogen molecules / electron.

The provision of a large pumping speed and the use of a known conductance ensure the validity of Equation (1) and Equation (2). Before and during ex-

posure to electrons, the pressure in the pumping chamber was always 7 to 10 times lower than the pressure in the test chamber.

The results presented in § 5 have been corrected for the background pressures derived from the partial pressures recorded before the irradiation.

4 Experimental Programme

Before installing the OFHC copper target on its support the sample was chemically cleaned with an alkaline detergent and passivated in a sulfochromic acid according to a standard CERN procedure⁴ [2]. The following program was applied :

- (1) Bakeout of the whole ESD setup. The test chamber was baked at 150 °C and the pumping chamber, including the Cf 150 valve, at a temperature of 250 °C. During the bakeout, the filaments of all vacuum gauges and of the electron filament were degassed. The temperature of the targets were respectively 120 °C for the copper target and 116 °C for the NEG target. The chosen temperature of 116 °C for the NEG is insufficient to achieve activation [4].
- (2) Irradiation of the copper target after cool down of the ESD setup. The base pressures before irradiation were $P_{test} = 8.10^{-11}$ Torr and $P_{pump} = 9.10^{-12}$ Torr. The label of this experiment from Figure 2 to Figure 4 is *Cu*.
The maximum temperature of the target reached during irradiation was 54 °C.
- (3) Irradiation at room temperature of the non activated NEG St 707 target. The base pressures before irradiation were $P_{test} = 9.10^{-11}$ Torr and $P_{pump} = 1.10^{-11}$ Torr. The label of this experiment is *NEG 0%*.
The maximum temperature of the NEG target during the irradiation was 54 °C.
- (4) Calibration of the RGA for ¹³C¹⁸O followed by a complete bakeout of the ESD system at 275 °C, except of the injection line and the manipulator which were baked at 150°C. The NEG was fully activated at 350 °C for ~20 hours [3] [4].
- (5) The NEG was irradiated at room temperature. The initial base pressures were 7.10^{-11} Torr for P_{test} , and 7.10^{-12} Torr for P_{pump} . The label of this experiment is *NEG 100%*.
The maximum temperature of the NEG target reached during irradiation was 52 °C.

⁴ omitting the usual perchloroethylene vapor degreasing operation.

- (6) The NEG was first activated and subsequently saturated with $^{13}\text{C}^{18}\text{O}$ at room temperature by exposure to a pressure of 6.10^{-2} Torr for 6 hours. The system was then evacuated using the turbomolecular pump and the ion pump assisted by the titanium sublimator. The base pressures before irradiation were $P_{test} = 10^{-10}$ Torr and $P_{pump} = 7.10^{-12}$ Torr. This experiment is referred to as *NEG (C13O18)*.

The maximum temperature of the NEG target reached during irradiation was 48 °C.

- (7) Finally the system was opened to air to replace the irradiated NEG target by a new sample. This new target was fully activated at 350 °C for ~20 hours. After cool down, the NEG was saturated by exposure to a pressure of 8.10^{-2} Torr of CO for 13 hours.

The system was again evacuated using the turbomolecular pump, the ion pump and the titanium sublimator. The base pressures before irradiation were $P_{test} = 2.10^{-10}$ Torr and $P_{pump} = 7.10^{-12}$ Torr. This experiment is referred to as *NEG (CO)*.

The maximum temperature of the NEG target reached during irradiation was 46 °C.

5 Results

The ESD yield η was computed using Formula (1) and Formula (2). The electron flux $\dot{\Gamma}$ was calculated from the electron current on the target.

Figures 2 to 6 represent the ESD yield of each molecular species for the different sets of experiments. Figure 7 displays the integral total number of *C*O molecules desorbed during the irradiation.

NEG (C13O18) CO refers to the carbon monoxide desorbed from a NEG surface saturated with $^{13}\text{C}^{18}\text{O}$.

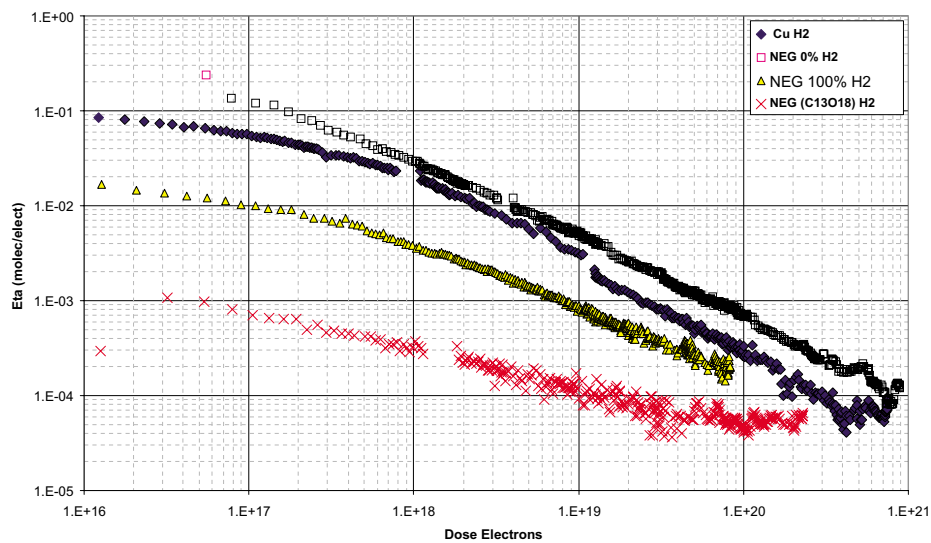


Figure 2. ESD yield of hydrogen for OFHC copper (Diamonds) and for NEG St 707, “as received” (Squares), activated at 100% (Triangles) and saturated with $^{13}\text{C}^{18}\text{O}$ (Crosses).

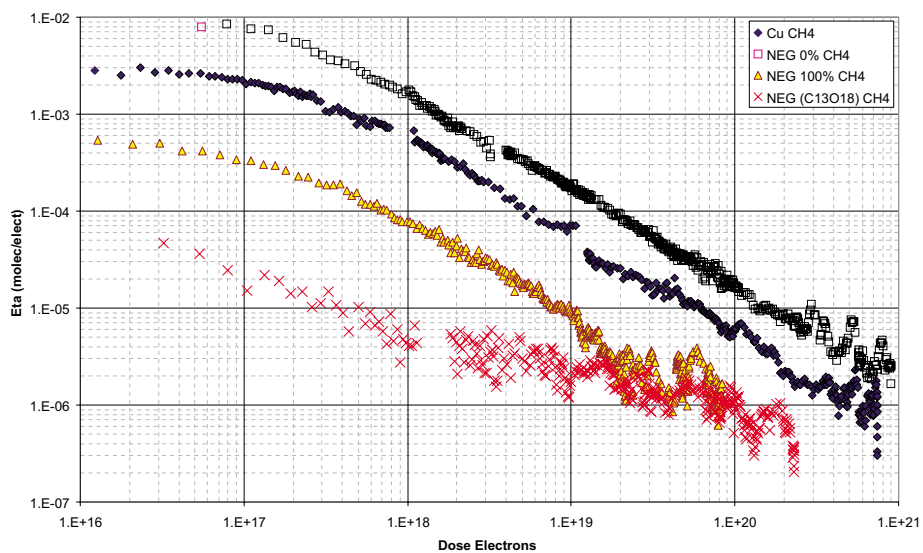


Figure 3. ESD yield of methane for OFHC copper and for NEG St 707, “as received”, activated at 100% and saturated with $^{13}\text{C}^{18}\text{O}$.

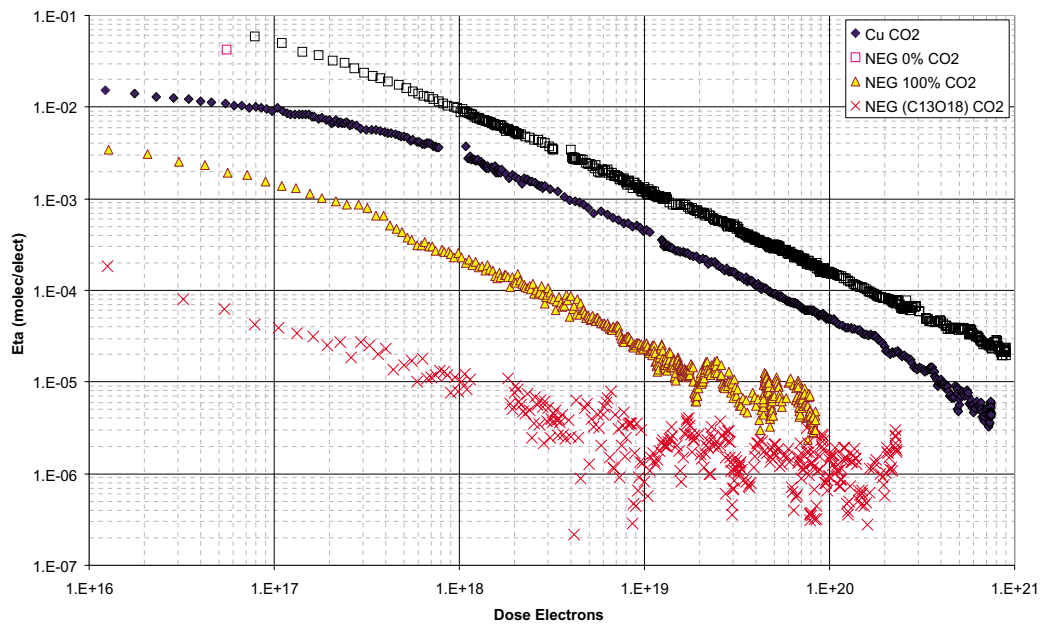


Figure 4. ESD yield of carbon dioxide for OFHC copper and for NEG St 707, “as received”, activated at 100% and saturated with $^{13}\text{C}^{18}\text{O}$.

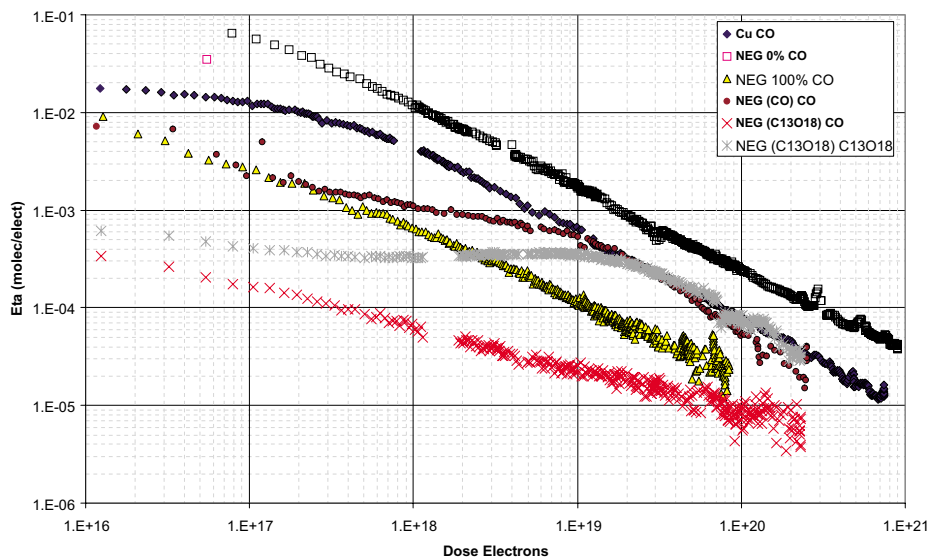


Figure 5. ESD yield of carbon monoxide & its main isotope for OFHC copper and for NEG St 707, “as received”, activated at 100%, saturated with CO (Circles) and saturated with $^{13}\text{C}^{18}\text{O}$ (Crosses; Asterisks).

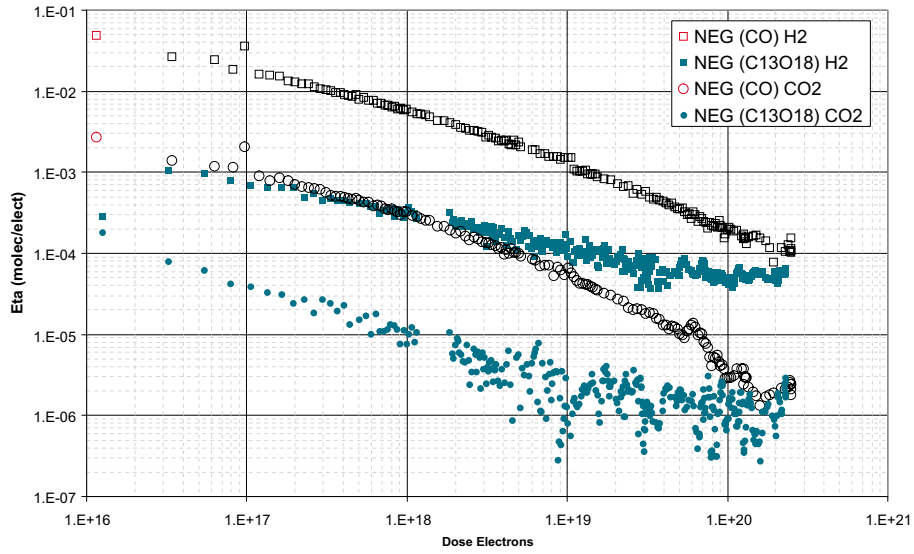


Figure 6. ESD yield of NEG St 707 saturated with CO (Empty Squares and Circles) and saturated with $^{13}\text{C}^{18}\text{O}$ (Full Squares and Circles).

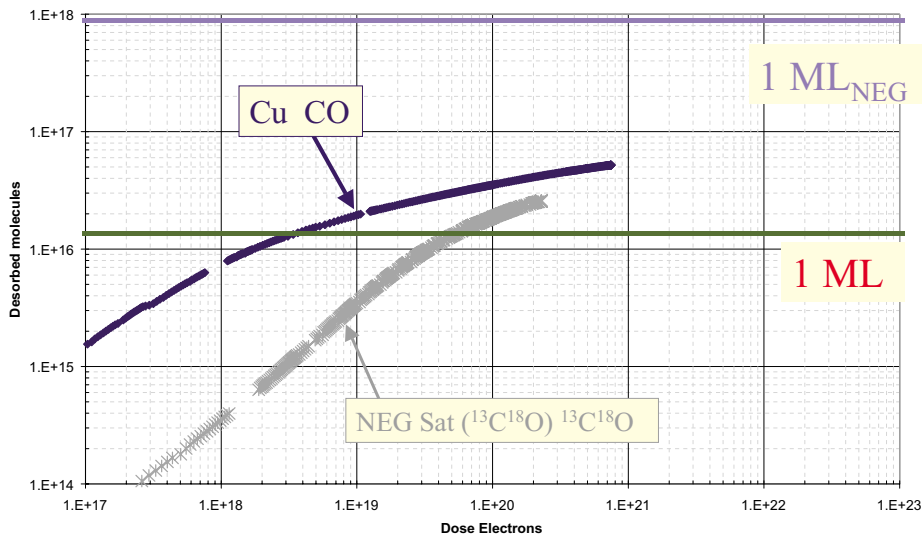


Figure 7. Total number of CO molecules desorbed from the OFHC copper target and of $^{13}\text{C}^{18}\text{O}$ molecules desorbed from the NEG St 707 saturated with $^{13}\text{C}^{18}\text{O}$.

6 Discussion

The interesting result of this study of ESD, as shown in the Figure 2 to 5 is the low desorption yield of the fully activated NEG as compared to the desorption yield of the 120 °C baked OFHC copper. The desorption yield of the fully activated NEG is found to be 5 to 10 times lower for CH₄, CO and CO₂ as compared to OFHC copper. The value for hydrogen is between 2 and 5 lower. The reduction factor between an activated NEG and an “as received” NEG is approximately 10, independent of the gas species.

The ESD yields of hydrogen, methane and carbon dioxide of a NEG saturated with ¹³C¹⁸O are lower than for baked OFHC copper as can be seen in Figures 2, 3 and 4. This same reduction is also observed in the case of a NEG saturated with CO, Figure 6 and [2]. It is found that at the beginning of the irradiation the ESD yield for CO of a NEG saturated either with CO or with ¹³C¹⁸O is significantly lower than for baked OFHC copper. During the irradiation this difference gradually disappears and the ESD yields become similar, Figure 5. It is also seen that at the beginning of the irradiation the behavior of the two isotopes is different. The ESD yield curve (Circles) of a NEG saturated with CO is above the curve for the NEG saturated with ¹³C¹⁸O (Asterisks). This observation also applies for the other gases, see Figure 6.

Inspecting the results for saturation by ¹³C¹⁸O, it is known from previous studies on Zr based NEG that CO occupies free adsorption sites and thus effectively inhibits the pumping of hydrogen and of other species [5] [7]. As an isotope ¹³C¹⁸O should behave as CO for chemical reactions and thus it can be expected that it will block the gettering effect of the St 707. Considering the inverse of this process, one would expect that also the desorption of a given species from a saturated NEG may be affected by the presence of other molecular species on the surface. The layer of adsorbed gas molecules on the saturated NEG surface may, therefore, not only prevent adsorption but also desorption of gas species other than of the pre-deposited molecules. From this model it would follow that for a CO saturated NEG surface the desorption yield of H₂, CH₄, CO₂ should be similar as for the fully activated NEG. This hypothesis can be verified in the case of saturation by CO, Figure 6 (empty squares and circles) as compared to Figure 2 and Figure 4 (Triangles). On the contrary, this hypothesis is not supported in the case of saturation by ¹³C¹⁸O.

Inspection of the measurements for the saturated NEG shows that at the end of the experiment, a leveling-off as well as some fluctuations of the data points appear. The plateau can be attributed to the lower limit of the resolution of the system, cf §3. The fluctuation of the data have been traced back to the changing liquid nitrogen level in the tank surrounding the titanium sublimator, which in turn leads to pressure changes in the system.

The experiments with $^{13}\text{C}^{18}\text{O}$ had their principal motivation in the interest to clearly distinguish between molecules pre-existing in the NEG and molecules used for controlled saturation of the surface. Another question of interest was to determine whether a recombination between isotopic atoms ^{13}C and ^{18}O and ordinary atoms present at the surface or originating in the bulk could take place.

It has been shown in [5] and [6] that CO is adsorbed dissociatively on a Zr surface. Following the hypothesis that $^{13}\text{C}^{18}\text{O}$ will behave as CO on the Zr surface, we have studied the masses between 2 to 50 *amu* to see if dissociated atoms of $^{13}\text{C}^{18}\text{O}$ would recombine with atoms from the bulk of the NEG and form molecules like $^{13}\text{CH}_4$ or others.

Indeed the residual gas spectra show peaks at masses 29 and 30 corresponding to ^{13}CO and C^{18}O . It was also possible to see traces of isotopic CO_2 . Unfortunately, a careful analysis of the injected gas subsequently revealed insufficient isotopic purity and confirmed that these gases were already present during the injection. Therefore, it was not possible to draw any definite conclusions from this part of the experiment [2].

The total number of molecules of the type $^*\text{C}^*\text{O}$ which are desorbed from a NEG sample saturated with $^{13}\text{C}^{18}\text{O}$ during an irradiation is shown in Figure 7. It is interesting to note that at the end of the irradiation it was not possible to desorb the equal amount of $^{13}\text{C}^{18}\text{O}$ molecules (Asterisks) which was initially deposited to saturate the NEG surface. This difference may be explained by the fact that the NEG has a very rough surface as compared to, e.g. copper and stainless steel. As an order of magnitude estimate, a roughness factor of $R \sim 60$ has been derived from pumping speed measurements with the NEG St 707 [3] and [8]. The total number of molecules for 1 mono layer (ML_{NEG}) on the 15 cm^2 irradiated area of the sample thus corresponds to $9 \cdot 10^{17}$ molecules⁵. This number should be compared to the measured $3 \cdot 10^{16}$ molecules which are desorbed during the irradiation, a quantity which is considerably less than for the copper sample as can be seen in Figure 7.

Two models can be invoked to explain on one hand this surprisingly low number of molecules desorbed from the NEG saturated with $^{13}\text{C}^{18}\text{O}$ and the relatively low ESD yield as compared to copper.

In a first model, one may invoke the porous structure of the St 707. In fact, the getter is obtained by sintering a powder of the ZrVFe alloy onto a metal substrate. The thickness of the getter alloy on the substrate is given as $70\ \mu\text{m}$ [4]. This method yields a very rough but also a very porous getter with a large effective surface area.

During the saturation of the activated getter molecules chemisorb not only

⁵ $1\ \text{ML} \sim 10^{15}\ \text{molecules cm}^{-2}$, $1\ \text{ML}_{NEG} = R \times 1\ \text{ML}$

on the top most surface but diffuse deeply inside the voids between grains to chemisorb on the large surface of these grains.

Since the penetration length in the alloy of the 300 eV electrons used for the irradiation is ~ 3.5 nm [9] only a small fraction of the layers closest to the surface will participate to the desorption process and hence a small fraction only of the total amount of deposited molecules is available for the desorption. In addition this porous structure may explain the relatively low desorption coefficients of the saturated NEG. Since molecules are trapped inside the confined space of the pores, they experience a large number of repeated desorption-adsorption cycles before escaping from the surface.

To understand the relatively low η as well as the small total number of $^{13}\text{C}^{18}\text{O}$ desorbed by ESD a second hypothesis invoking enhanced diffusion of atoms inside the getter alloy has been considered.

To estimate the contribution of this effect, an analogy can be made with the thermal activation process. During activation at temperatures between 300 °C and 400 °C, corresponding to an energy range between 0.05 eV and 0.06 eV, the adsorption sites located on the NEG surface become “free” of adsorbed molecules. During activation surface atoms diffuse into the bulk to minimize their potential energy and accumulate inside the getter. In this way molecules become effectively inaccessible to ESD and the clean surface exhibits a low ESD yield. It is plausible that the same process may occur during ESD due to the energy deposited by the 300 eV electrons. In this model electrons would act as thermal activators rather than as inefficiently transferring momentum directly to the diffusing molecules. To verify this hypothesis the evolution of the depth profile of the molecular concentration close to the NEG surface might be studied using Auger analysis [2]. A conclusive demonstration of this concentration profile should be the subject of future work.

7 Conclusion

This study has shown that a fully activated NEG has a very low ESD yield and desorbs in total significantly less gas than a baked OFHC copper surface. Even after complete saturation with CO or $^{13}\text{C}^{18}\text{O}$ the NEG maintains a lower initial ESD yield for these species than baked copper. Nevertheless, during extended bombardment the ESD yields of both surfaces approach the same value after a dose of $1 \cdot 10^{19}$ electrons.

During extended irradiation of the NEG it was not possible to remove entirely the pre-deposited $^{13}\text{C}^{18}\text{O}$ molecules. The dominant part of the gas taken up during the saturation has remained on the getter and was inaccessible to ESD. The relatively low ESD yield of the NEG and this striking failure of the re-

removal of molecules from the surface may be attributed to the porous surface structure of the St 707 but also to the alternative possibility that molecules diffuse inside the NEG during the irradiation. These two hypotheses should be clarified by further dedicated experiments. This goal could be achieved by varying the getter structure using thin film getters, which are currently developed at CERN[10].

Saturating a getter with $^{13}\text{C}^{18}\text{O}$ gas of high isotopic purity could provide conclusive evidence about the so far only speculated recombination processes on the surface. SIMS analysis with the potential to differentiate between isotopes may give a more reliable answer than Auger analysis to the question of atomic diffusion inside the NEG during electron irradiation.

The integral number of molecules desorbed during the irradiation of getters with different surface roughness should be an important parameter to optimise the getter performance in terms of pumping capacity and ESD yield.

Depending on the specific application in an accelerator vacuum system like the LHC, where surfaces are exposed to electron as well as to photon bombardment, getters could provide an interesting advantage compared to more conventional materials like stainless steel or copper.

8 Acknowledgments

We would like to thank H. Kos for his help in making the ESD manipulator operational.

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