ISBN: 978-3-95450-247-9 ISSN: 2673-5490 doi: 10.18429/JACoW-IPAC2024-THBN3

LIFETIME OF NON-EVAPORABLE GETTER THIN FILMS OVER REPEATED ACTIVATION

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Abstract

This paper reports a preliminary study of the degradation of non-evaporable getter (NEG) coatings over a series of activations and saturations. At Daresbury Laboratory, two samples were grown and installed in a dedicated facility for evaluating pumping properties. For each sample, activation was repeated to the same temperature for 16 cycles, between which the coatings were saturated with a mixture of CO and H_2 at a pressure of (1-2)×10^{-2} mbar. A decrease in pumping properties was observed, with a larger effect seen at higher temperatures and for H_2. This work is still ongoing, and more results will be reported in the future.

INTRODUCTION

Particle accelerators are continually being improved and replaced with more powerful and capable facilities. However, with the new generation of accelerators, there is an ever-increasing goal of improved sustainability; lower operating costs and smaller environmental impact is an important factor when putting forward proposals for new machines.

One potential improvement relates to narrower beam sizes that allow the aperture of the beam chamber to be reduced and magnets with smaller gap employed, thus reducing the size and operating costs. However, a reduced beam chamber aperture makes it harder to reach UHV/XHV conditions, as vacuum conductance is reduced. A solution to this is non-evaporable getter (NEG) coating of the beam chamber [1-5]. This provides both a diffusion barrier for H_2 between the chamber walls and the vacuum, and also distributed pumping along the length of the beamline. They have been used successfully in accelerators such as the LHC and MAX IV [5-7].

Understanding and improving NEG coatings can help to increase the sustainability of accelerators. For a NEG coating to provide pumping, it must be baked to activate the surface. As NEG coatings have been improved, these activation temperatures have been lowered from 180-300 °C to 160-200 °C, with onset of pumping at 140 °C also being proven achievable [5-13]. Lower temperatures mean lower energy requirements, but also a greater flexibility in accelerator design. The range of suitable materials increases with the reduced temperature requirement, as well as needing to design for less thermal expansion, meaning less bellows are needed throughout the accelerator. The activation process has also been shown to be improved by increasing activation duration. If lower activation temperature is desired, this could be done with a longer activation duration to maintain pumping properties [12].

The activation of NEG coatings takes place as the surface is changed from the oxide to the metallic state, providing absorption sites that can then act as pumps. Over time, under certain conditions (e.g. a leak or highly outgassing beam chamber components) all the absorption sites on the NEG surface become saturated, i.e. its sorption capacity is reached, and it is no longer an effective pump. At this point it must be reactivated.

Over the lifetime of a NEG coating, it will undergo the process of activation and saturation repeatedly, each time diffusing more molecules into the area below the surface, both from the surface monolayer and molecules within the substrate. In contrast to NEG cartridges, NEG coatings have very limited sorption capacity, and once oxygen solubility is reached, NEG activation will cease. With each saturation, the NEG is closer to limit, with less available space for diffusion leading to deterioration of the NEG pumping capability, with lower performance for the same activation procedure.

The effect of NEG coatings pumping properties degradation after repeated activation-air venting cycles was studied at CERN [3] and GSI [6]. Degradation of H_2 and CO pumping speed and capacity were observed after each cycle, after 5-6 vents a higher activation temperature required to achieve better pumping speed and capacity.

This study looks at two samples each activated 15 times at 160 and 200 °C respectively, both tubes used in the study were coated with columnar TiVZr. The pumping properties were measured after each activation, to determine the lifetime of the coating.

SAMPLE PREPARATION

The cylindrical magnetron deposition facility used at Daresbury Laboratory is described in detail in ref. [12]. For each deposition, a TiVZr target was used, created by twisting a 1 mm wire of each metal together. Each sample tube had 0.5 m length and 35 mm inner diameter. Sample S1 was made of aluminium and sample S2 was made of 316 LN stainless steel. A DC power supply was used, and krypton gas injected to make the plasma. Table 1 shows the deposition parameters used for the coating.

Table 1: Deposition Parameters of NEG Coated Samples

Parameter	S1-Al	S2-SS
Gas	Kr	Kr
Target	TiVZr	TiVZr
Duration	3 hrs 45m	5 hrs
Pressure (mbar)	8.5 × 10^{-2}	8.6 × 10^{-2}
Power (W)	75	75

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During both depositions, witness samples made of copper foils were placed above and below the sample tube, coated with it and used for analysis. A scanning electron microscope (SEM) was used to obtain images of the microstructure from the witness samples, these images can be seen for S1 (Fig. 1) and S2 (Fig. 2). It shows a mostly columnar coating, dense areas. A dense structure has a low void volume due to compactness of the film. The higher energy of arriving atoms on the surface gives it higher probability of occupying sites with higher surface energy. These act as good barrier layers as there are few easy paths of diffusion.

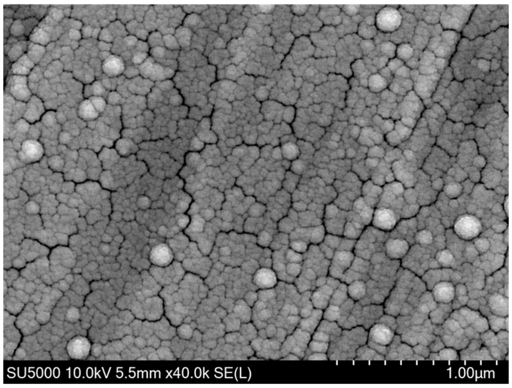

Figure 1: SEM image of sample S1.

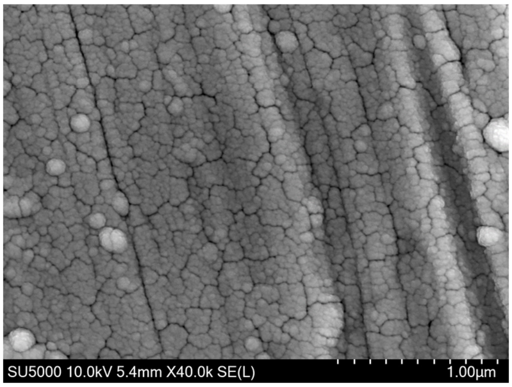

Figure 2: SEM image of sample S2.

Columnar structure results from lower energy impacts leading to vertical columns of particles forming the coating, while a poorer barrier, this increases surface area available for pumping.

The samples were then analysed using energy-dispersive X-ray spectroscopy (EDS), giving their composition, shown in Table 2. Copper is present as the foil beneath the coating is detected, a greater percentage of Cu is seen in S1 as the coating is thinner due to the reduced time. More samples will be produced to further assess the effect of sample thickness.

Table 2: EDS Analysis of Surface Composition

Element	S1(at. %)	S2 (at. %)
Cu	31.88	1.93
Ti	24.02	23.04
V	31.38	48.00
Zr	12.71	27.03

EXPERIMENTAL PROCEDURE

The experimental procedure for measuring the pumping properties of a NEG coated tube is described in refs. [5, 14]. NEG coated samples are activated using a two-step procedure. First, the test system was baked, and the extractor gauge (EG) and residual gas analysers (RGAs) degassed at the end of bakeout to pump away all contaminants from the vacuum system, while the NEG coated vessel was held at 80 °C. Then the vacuum system was cooled to room temperature and the NEG coating was activated to a desired temperature for 24 h.

After activation, the system was left under UHV pumping overnight before commencing the gas injection to ensure everything was fully cooled. A pressure in the range of $1\times10^{-10} – 1\times10^{-9}$ mbar was achieved.

In this study, pumping properties were measured by injecting a gas mixture of H_2 and CO at a ratio of 1:9.

The gas mixture was initially injected at one end of the NEG coated vessel to reach $(1\text{-}3)\times10^{-8}$ mbar, and then steadily increased to $(1\text{-}3)\times10^{-6}$ mbar. This pressure was held until CO saturation is reached, regarded as the point where the two RGAs measure the same partial pressure of CO.

During injection, the RGAs measure the partial pressures P_1 and P_2 at both ends of the vessel. The partial pressure ratio ($R = P_1/P_2$) is calculated for each gas and can be used to find the sticking probability (α), defined as the ratio of particles absorbed by the surface to the number of particles hitting this surface. The NEG coating sorption capacity (C), defined as the number of particles that can be absorbed onto the surface of the NEG coating before it is saturated, is also obtained from the gas injection. As it is difficult to identify when saturation is complete during the experiment, capacity is measured at a specific value of R. This property is only comparable between samples of the same dimensions, as it is dependent on sample geometry.

Once the experiment was completed, the RGAs and EG were switched off, and the remaining gas mixture was released into the test chamber and held for 30 minutes. The pressure during this time was $(1\text{-}3)\times10^{-2}$ mbar which ensured full saturation of the NEG with CO. This is considered a small leak saturation, as opposed to a full vent to air as carried out in [3, 6]. External pumping then recommenced, the RGAs and EG were switched on, and reactivation could begin. In total, 15 consecutive activations were performed for S1 and S2 using 160 and 200 °C temperatures respectively.

RESULTS

The results are plotted as the ratio of partial pressure vs the number of molecules injected per m^2. The initial partial pressure ratio is taken as an average of the first 5 points after injection. This ratio is then converted to sticking probability (α) using the results of a test particle Monte-Carlo (TPMC) model of the system created with MOLFLOW+ [15, 16]. The procedure to obtain α is described further in refs. [11, 14]. However, this method is most reliable for sticking probability $0.002 \le \alpha \le 0.1$. For $\alpha < 0.002$, the error is so high the TPMC model is not usable [15]. As the H_2 sticking probability lies around this range, another method needed to be used. Instead, sticking probability was calculated using eq. (1):

$$\alpha = \frac{4Q}{A\bar{v}P} \qquad (1)$$

where Q is the gas flow rate into the chamber, A is the surface area of the NEG coated sample, $\bar{v}$ is the velocity of the molecules and P is the partial pressure in the chamber. Here, P is taken as the average between the two RGAs:

$$P = (P_1 + P_2)/2. \qquad (2)$$

The results for sticking probability for both H_2 and CO are shown in Fig. 3.

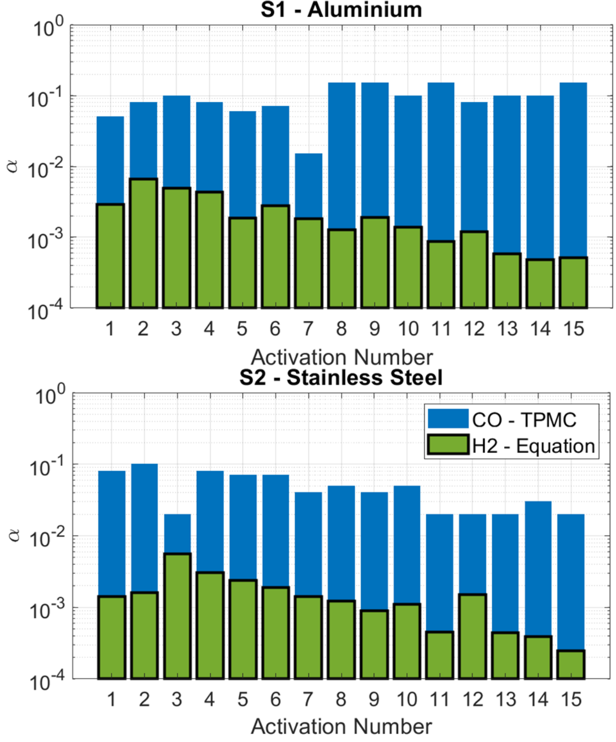

Figure 3: α_{H2} and α_{CO} for each activation of sample S1 and S2.

The CO sorption capacity (C_{CO}) is defined here as the number of injected molecules per area [CO/m^2] at R=10, the results of this for both samples are shown in Fig. 4. Capacity cannot be found for H_2 as there is never a large enough ratio.

DISCUSSION

For both samples, α_{H2} starts off comparable to previous measurements from other studies with similar coatings [5], starting from α_{H2}=2.9×10^{-3} for S1 and α_{H2}=1.4×10^{-3} for S2. These both drop to below α_{H2}= 5×10^{-4} by the 15th activation. For CO, the sticking probability is also as expected, but does not show the fast degradation seen for H_2. For S1, degradation is not apparent, while for S2, α_{CO} drops from roughly α_{CO}=0.1 to 0.02 for the last four activations.

Even if α_{CO} was not affected significantly by repeated activation cycles, there is a clear decrease in the CO sorption capacity with each activation. For S1, C_{CO} falls from a peak of 5×10^{18} to 1.4×10^{18} CO/m^2, for S2 the fall was from 6.7×10^{18} to 1×10^{18} CO/m^2. Again, degradation is more pronounced in S2.

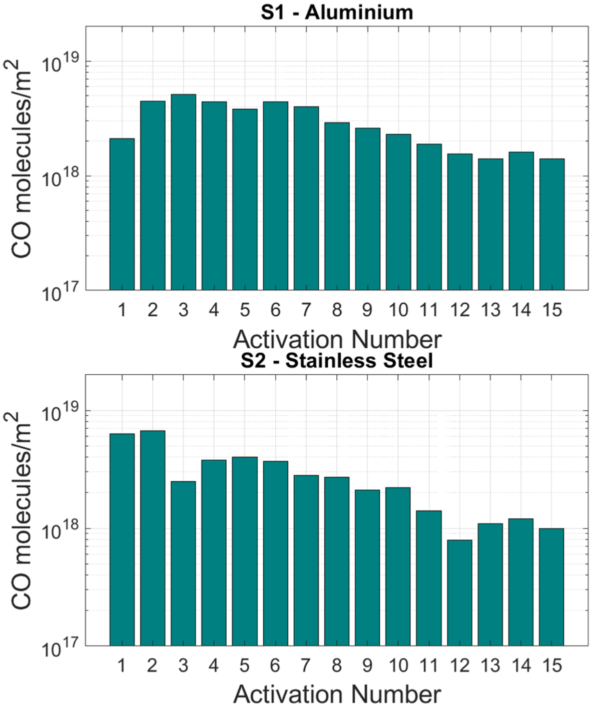

Figure 4: C_{CO} at R=10 for each activation of sample S1 and S2.

H_2 pumping degrades faster than CO pumping can be attributed to the greater concentration of H_2 in the bulk material beneath the NEG coating. During activation, this is able to diffuse towards the surface, reducing the amount of available space for H_2 absorption from the injected gas.

Meanwhile, the greater deterioration of CO pumping in S2 compared to S1 may be attributed to activation temperature. A higher temperature promotes more diffusion, while this in beneficial for clearing the surface monolayer of residual gasses more efficiently at the same time, it also allows greater diffusion within the bulk, accelerating the process of saturating the area beneath the surface. As the samples have a few differences, this can only be hypothesised more samples will be created to expand the study.

CONCLUSION

Two NEG coated samples were activated over a series of 15 activations to the same temperature, 160 °C for S1 and 200 °C for S2. NEG coatings lose their pumping efficiency by a factor 6 for H_2 on S1, with no decrease for CO and by a factor 9 for H_2 and a factor 4 for CO on S2. The process is heightened for H_2 compared to CO, mostly likely due to a higher H_2 content within the bulk material on which the NEG coating is deposited.

These results provide useful information on partial venting of NEG coatings and shows that these coatings will maintain pumping properties over at least 15 saturation and activation cycles without the need to increase activation temperature.

REFERENCES

[1] C. Benvenuti, P. Chiggiato, F. Cicoira, and V. Ruzinov, "Decreasing surface outgassing by thin film getter coatings," *Bull. Soc. Vac. Coaters*, vol. 50, no. 1–2, pp. 57–63, May 1998. `doi:10.1016/s0042-207x(98)00017-7`

[2] C. Benvenuti *et al.*, "A novel route to extreme vacua: the non-evaporable getter thin film coatings," *Bull. Soc. Vac. Coaters*, vol. 53, no. 1–2, pp. 219–225, May 1999. `doi:10.1016/s0042-207x(98)00377-7`

[3] C. Benvenuti *et al.*, "Vacuum properties of TiZrV non-evaporable getter films," *Bull. Soc. Vac. Coaters*, vol. 60, no. 1–2, pp. 57–65, Jan. 2001. `doi:10.1016/s0042-207x(00)00246-3`

[4] C. Benvenuti, A. Escudeiro Santana, and V. Ruzinov, "Ultimate pressures achieved in TiZrV sputter-coated vacuum chambers," *Bull. Soc. Vac. Coaters*, vol. 60, no. 1–2, pp. 279–284, Jan. 2001. `doi:10.1016/s0042-207x(00)00389-4`

[5] O. B. Malyshev. "Non-evaporable Getter (NEG)-Coated Vacuum" (Chapter 5) in *Vacuum in Particle Accelerators: Modelling, Design and Operation of Beam Vacuum Systems*, Wiley, 2019.

[6] M. Bender, H. Kollmus, M. C. Bellachioma, and W. Assmann, "UHV-ERDA investigation of NEG coatings," *Nucl. Instrum. Methods Phys. Res., Sect. B*, vol. 268, no. 11–12, pp. 1986–1990, Jun. 2010. `doi:10.1016/j.nimb.2010.02.114`

[7] P. Manini, A. Bonucci, A. Conte, and S. Raimondi, "Deposition of Non Evaporable Getter (NEG) Films on Vacuum Chambers for High Energy Machines and Synchrotron Radiation Sources", in *Proc. EPAC'06*, Edinburgh, UK, Jun. 2006, paper TUPCH178, pp. 1435-1437.

[8] *"*MAX IV Facility Detailed Design Report". (n.d.). 2014

[9] R. Valizadeh, O. B. Malyshev, J. S. Colligon, A. Hannah, and V. M. Vishnyakov, "Comparison of Ti-Zr-V nonevaporable getter films deposited using alloy or twisted wire sputter-targets," Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, vol. 28, no. 6, pp. 1404–1412, Nov. 2010. `doi:10.1116/1.3504600`

[10] O. B. Malyshev, R. Valizadeh, and A. N. Hannah, "Pumping properties of Ti–Zr–Hf–V non-evaporable getter coating," *Bull. Soc. Vac. Coaters*, vol. 100, pp. 26–28, Feb. 2014. `doi:10.1016/j.vacuum.2013.07.035`

[11] R. Širvinskaitė, O. B. Malyshev, R. Valizadeh, A. Hannah, and M. D. Cropper, "Single metal zirconium non-evaporable getter coating," *Bull. Soc. Vac. Coaters*, vol. 179, p. 109510, Sep. 2020. `doi:10.1016/j.vacuum.2020.109510`

[12] E. A. Marshall, O. B. Malyshev, and R. Valizadeh, "The Effect of Activation Duration on the Performance of Non-Evaporable Getter Coatings", in Proc. IPAC'22, Bangkok, Thailand, Jun. 2022, pp. 2854-2857. `doi:10.18429/JACoW-IPAC2022-THPOTK039`

[13] O. B. Malyshev *et al.*, "Influence of deposition pressure and pulsed dc sputtering on pumping properties of Ti–Zr–V nonevaporable getter films," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 27, no. 3, pp. 521–530, Apr. 2009. `doi:10.1116/1.3112623`

[14] Y. Gao *et al.*, "Effect of the film thickness on electron stimulated desorption yield from Ti-Zr-V coating," *IEEE Open J. Instrum. Meas.*, vol. 17, no. 08, p. P08025, Aug. 2022. `doi:10.1088/1748-0221/17/08/p08025`

[15] R. Kersevan and M. Ady, "Recent Developments of Monte-Carlo Codes Molflow+ and Synrad+", in *Proc. IPAC'19*, Melbourne, Australia, May 2019, pp. 1327-1330. `doi:10.18429/JACoW-IPAC2019-TUPMP037`

[16] O. Seify, A. N. Hannah, O. B. Malyshev, R. Sirvinskaite, and R. Valizadeh, "Test Particle Monte Carlo Simulation of NEG Coated Narrow Tubular Samples", in *Proc. IPAC'18*, Vancouver, Canada, Apr.-May 2018, pp. 3862-3864. `doi:10.18429/JACoW-IPAC2018-THPAL092`