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Vacuum properties of TiZrV non-evaporable getter films

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Abstract

Sputter-deposited thin films of TiZrV are fully activated after 24 h "in situ" heating at 180 °C. This activation temperature is the lowest of some 18 different getter coatings studied so far, and it allows the use of the getter thin film technology with aluminium alloy vacuum chambers, which cannot be baked at temperatures higher than 200 °C.

An updated review is given of the most recent results obtained on TiZrV coatings, covering the following topics: influence of the elemental composition and crystal structure on activation temperature, discharge gas trapping and degassing, dependence of pumping speed and surface saturation capacity on film morphology, ageing consequent to activation-air venting cycles and ultimate pressures. Furthermore, the results obtained when exposing a coated particle beam chamber to synchrotron radiation in a real accelerator environment (ESRF Grenoble) are presented and discussed.

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1. INTRODUCTION

In the framework of the Large Hadron Collider (LHC) project, at the end of 1995 an activity was started at CERN with the aim of producing non-evaporable getter thin films. If used to coat the inner walls of a vacuum chamber, these films could transform a chamber from a gas source to a pump when activated during the vacuum system bakeout, thereby providing an elegant and effective solution for pumping conductance limited vacuum systems, such as those of particle accelerators. In order to be suitable for this application, the coatings should display an activation temperature compatible with the usual baking temperatures, i.e. not higher than 400 °C for stainless steel vacuum chambers and 200 °C for chambers made of aluminium alloys as envisaged for the LHC experimental areas.

Within a few months many coatings of different composition were produced, offering activation temperatures lower than 400 °C [1, 2]; at the end of 1997 a ternary alloy of titanium, zirconium and vanadium was found to display full activation after 24 h heating at 200 °C [3]. Detailed studies of this alloy have since been made to obtain a complete understanding, and possibly also further improvements, of its vacuum properties.

The study has been focussed on the following aspects:

- influence of the elemental composition on activation temperature;
- sticking factors for H_2 and CO;
- room temperature saturation capacity for CO;
- dependence of the vacuum performance on the activation-air venting cycles;
- trapping of discharge gas atoms and their release during the various stages of the vacuum cycle;
- testing of a coated chamber in a real accelerator environment.

The results of this study are described below. The discussion of the material selection criteria, the description of the production and of the adopted characterization techniques and the initial results may be found in ref. [1, 2, 3].

2. ACTIVATION TEMPERATURE

To overcome the difficulty of purchasing the desired alloys, the cathodes were initially made by intertwisting elemental wires, readily available on the market [1]. The inconvenience of this approach is that it only allows varying the composition of the resulting coating in a discontinuous way, by varying the number and/or the size of the wires of each element. In the case of the TiZrV films, a wire of the same diameter for each of the three elements has been used, resulting in the composition Ti 30 %, Zr 20 % V 50 % (atomic percentages). This coating was found to display full activation after 24 h heating at 200 °C [3]. To obtain a more precise value of the activation temperature, the interval between 150 °C and 200 °C has been explored, showing that activation is indeed complete after 24 h heating at only 180 °C (see Fig. 1).

During sputtering the cathode temperature may exceed 1000 °C. Above this temperature both Ti and V may present non negligible vapour pressures, resulting in a higher deposition rate with respect to Zr, of which the vapour pressure is much lower. For this reason the actual composition of the coating may depend on the sputtering parameters (cathode diameter, sputtering rate, sputtering pressure). In order to study the influence of the elemental composition of the TiZrV alloy on its activation temperature, a dedicated coating system has been built and samples of different composition have been produced [4]. The activation process taking place while increasing the temperature of samples has been monitored by Auger Electron Spectroscopy (AES). Heating favours the increase of the metallic Zr peak with respect to the Zr oxide peak. It has been assumed that different samples have reached the same level of activation

when their relative increase of this peak is the same. This allows defining zones which group samples of equal activation temperature in the composition diagrams as shown in Fig. 2 [4]. These results show that the activation temperature minimum is available over a broad range of compositions, characterized by a relatively low Ti content.

X-ray analysis indicates that the low activation temperature is linked to amorphous or nanocrystal structure, which particularly enhances oxygen diffusion along grain boundaries. A full description of these results is given elsewhere in this conference [4].

The 3-cathode sputtering system also allows coating disks of larger dimensions which may be used for sticking factor measurements. For this purpose the disks are installed on the pump port of a pumping speed measuring dome. Being experimentally more time consuming than AES sample analysis, this evaluation method will be applied to only a limited selection of alloy compositions.

3. STICKING FACTORS AND SURFACE CAPACITY

Since the beginning of this activity some 18 different coatings have been produced and tested. After complete activation the measured sticking factors range between 6×10^{-3} and 5×10^{-2} for H_2 and between 0.4 and 0.8 for CO. This spread closely corresponds to that reported in the literature [5] for titanium films deposited "in situ" by sublimation; it cannot therefore be imputed to the chemical composition or to variable surface cleanliness of the coatings.

Surface roughness play an important role in the definition of the molecular sticking factors. Multiple reflections may take place when a molecule hits a rough surface, and its capture probability is enhanced correspondingly. Among the different coatings tested until now, the TiZrV films present the lowest sticking factors and also the smoothest surface. A rough surface also provides a larger number of adsorption sites per unit of geometric area. A precise quantitative evaluation of the film roughness may indeed be obtained by measuring the quantity of a gas (such as CO not diffusible at room temperature) required to saturate the getter film. The TiZrV coatings also provide the lowest saturation capacity among the tested materials, as shown in Fig. 3, where the CO pumping characteristics of the TiZrV coating are compared to that of a coating with a very rough surface. The TiZrV displays a reduced initial pumping speed, i.e. a low sticking factor, and a saturation capacity lower by about 2 orders of magnitude.

The roughness of a coating may depend not only on its chemical nature, but also on the sputtering parameters and on the nature of the substrate. An example of the substrate influence is given in Fig. 4, where TiZrV films deposited under similar conditions on various substrates are shown. While copper and stainless steel favour a very smooth TiZrV film surface, aluminium and beryllium produce a "cauliflower" type structure.

Even for the most unfavourable coating and substrate combinations, the roughness of a film may always be enhanced by roughening the surface of the substrate prior to coating. A specific surface area increase of about one order of magnitude has been obtained for TiZrV coatings in this way, and the optimization of the method is still going on. The strategy of improvement consists in providing a large substrate surface area without creating hidden regions inaccessible to the sputtered atoms. By combining adequate substrate and coating materials and substrate treatments, initial sticking factors and total surface capacities equal to those provided by the St 707 strip produced by SAES getters have been obtained, in spite of the much smaller thickness (by a factor 10 to 25) of the sputter-coated film

4. ULTIMATE PRESSURE

Many different vacuum chambers have been coated with TiZrV films for various purposes, and they all have been tested in the following way. The chamber is connected to a vacuum system pumped by a sputter-ion and a Ti sublimation pump (liquid N_2 cooled), via an

orifice providing a conductance of 25 ls^{-1} for H_2 [1]. This vacuum system is pumped during baking by a turbomolecular pumping station and after baking reaches a pressure in the low 10^{-12} Torr range. At the other extremity of the chamber a CERN type Helmer gauge [6] is installed inside its own stainless steel housing. To minimize the influence on the Helmer gauge reading of the gas entering the chamber through the connecting orifice, the length of the chambers is important (standardized at 2 m). The chamber is heated after baking at progressively higher temperatures and after each heating cycle the ultimate pressure is measured. Then H_2 is injected in the vacuum system and the pressure drop across the chamber is measured, so as to derive the gas sticking factor on the coated surfaces by Monte Carlo simulation. Full activation is reached when both sticking factors and ultimate pressure become insensitive to a further chamber heating at higher temperature.

While, after full activation, all chambers coated and tested in the same way display very similar sticking factors, a large ultimate pressure spread is obtained. If the pressure gauge is a reproducible source of gas, the measured ultimate pressure cannot be lower than the ratio of the gauge degassing rate to the pumping speed of the chamber at the gauge location. For constant sticking factors, this pumping speed increases with the square of the chamber diameter, and consequently larger chambers should provide a lower ultimate pressure, as observed. In order to render this qualitative conjecture more quantitative, the degassing rate of the gauge (inserted in its housing) has been measured on a different system, and the ultimate pressure generated by this degassing has been plotted versus the applied pumping speed. This variation is shown in Fig. 5, together with the experimental data. From this figure it may be concluded that the measured pressures are an instrumental artefact consequent to the degassing of the measuring instrument. Much lower pressures would be obtained (but not measured!) in the absence of the gauge. Lower pressures are actually present further away from the gauge, where the interposed chamber length provides a more effective pumping for the gauge degassing.

The reported experimental data cover the pressure range from 10^{-12} down to 10^{-13} Torr and chamber diameters of 34 mm, 58 mm and 100 mm. Larger chambers (160 mm) have also been measured, but in this case the measuring uncertainty becomes larger and the pretended linearity shown in Fig. 5 is more questionable. The above conclusions substantiate an hypothesis formulated a few years ago, when ultimate pressures in the 10^{-14} Torr range were reported [7].

A more detailed description of this study is given elsewhere in this conference [8].

5. AGEING CONSEQUENT TO ACTIVATION-AIR VENTING CYCLES

During the activation process, the oxygen present in the surface passivation layer is diffused inside the getter film. Owing to the small film thickness (micrometer range) each such process results in a non negligible increase of the film oxygen concentration, which in turn may produce a deterioration of film performance (reduced pumping speed and capacity and increased activation temperature).

The effect of repeated activation-air venting cycles on the sticking factor of H_2 is shown in Fig. 6. The H_2 sticking factor has been chosen for this purpose because it is the most sensitive indicator of the film performance deterioration. A 5 µm thick TiZrV film is repeatedly activated and vented. The activation is initially carried out at 200 °C, and the activation temperature is progressively increased according to the progressive decrease of the H_2 sticking factor. From the results of Fig. 6 it may be concluded that film deterioration may be effectively counteracted over more than 25 cycles provided that the heating temperature is increased up to 350 °C.

Preliminary measurements indicate that film ageing may be reduced by dry air venting. However further tests are required to draw definite conclusions on this point.

6. DISCHARGE GAS TRAPPING AND DEGASSING

Energetic discharge gas neutrals impinging on the cathode may conserve a large fraction of their kinetic energy when bouncing back from the cathode and may be implanted in the growing film [9]. This process is particularly important when the atomic weight of the cathode material is higher than that of the discharge gas, and may be strongly reduced by using heavier gas for the discharge. For example, sputter grown Nb films contain about 400 ppm of argon, but using krypton as a discharge gas the trapped amount decreases to a few ppm only [10].

Since the release of rare gas during the various phases of the operating cycle may spoil the vacuum obtained particularly as rare gases are not pumped by getters, both the total gas content and its release have been carefully evaluated.

The rare gas content has been measured by laser ablating or melting a known amount of getter film and measuring the total amount of rare gas evolved in the process. A large number of materials have been sputtered using different discharge gases. The gas trapping has been found to be defined in first approximation by the momentum exchange at cathode impact as expected [9] but a dependence on the film crystal structure has also been found. The obvious conclusion in any case is that to reduce this effect krypton represents a better choice than argon. In the case of TiZrV coatings produced by using the intertwisted wire an argon content of about 3500 ppm has been measured while for krypton the content is lower by two orders of magnitude. In both cases the room temperature degassing after activation provides a negligible contribution to the ultimate pressure. A full account of the results is given elsewhere in this conference [11].

7. TESTING IN A REAL ACCELERATOR ENVIRONMENT

A 2 m long, 60 mm diameter stainless steel chamber coated with a TiZrV film has been installed on a dedicated beam line at ESRF – Grenoble. The measuring set-up follows the usually adopted scheme for synchrotron radiation induced degassing measurements [12]. Details of the experiment and a complete description of the results are presented elsewhere in this conference [13]. The main results are given in Fig. 7. Here a dramatic decrease (by about a factor 380) of the radiation induced pressure rise is shown after a 20 h heating of the chamber at 250 °C. The chamber has then been exposed to a total dose of about 10^{24} photons/m without showing any performance deterioration.

8. CONCLUSIONS

Many getter coatings were produced which undergo activation when heated at temperatures lower than 400 °C. The lowest activation temperature (180 °C for 24 h heating) has been recorded for TiZrV films over a wide range of compositions.

Although the quest for low activation temperature materials is still carried out empirically and predictive guide rules are still missing, good progress was achieved in the understanding of the coatings behaviour along the following lines.

- Small crystal size favours the activation; the lowest activation temperatures are obtained with amorphous and/or nanocrystal structures.
- Both the sticking factors and the total surface capacity of fully activated coatings depend only on surface roughness, which may be controlled to a large extent.
- No intrinsic limitations of ultimate pressure have been found. The measured values down to 10^{-13} Torr are an instrumental artefact due to the measuring gauge degassing. Much lower pressures certainly exist inside the coated chambers far away from the gauge.
- The ageing of the TiZrV coatings may be counteracted by increasing the activation temperature. The acceptable number of these cycles depends on the tolerable

performance deterioration for any given application. Dry air should be preferred to normal laboratory air for venting.

- The discharge gas trapping mechanism is well understood and the means of reducing the trapped gas amount so as to render its vacuum degassing negligible are mastered.
- Under synchrotron radiation bombardment the behaviour of getter coatings is consistent with that observed in the laboratory by electron bombardment, without any high dose deterioration.

In conclusion we estimate that the available experimental evidence and understanding allow using TiZrV coatings for the most stringent applications, provided that frequent ventings to air are not required.

References

1. C. Benvenuti, P. Chiggiato, F. Cicoira and Y, L'Aminot, *J. Vac. Sci. Technol*., 1998, A 16, 148.
2. C. Benvenuti, P. Chiggiato, F. Cicoira and V. Ruzinov, *Vacuum*, 1998, 50, 57.
3. C. Benvenuti, J.M. Cazeneuve, P. Chiggiato, F. Cicoira A. Escudeiro Santana, V. Johanek, V. Ruzinov and J. Fraxedas , *Vacuum*, 1999, 53, 219.
4. A. Prodromides, C. Scheuerlein and M. Taborelli, Proceedings of EVC-6, Lyon 1999.
5. P.A. Redhead, J.P. Hobson and E.V. Kornelsen, The Physical Basis of Ultrahigh Vacuum (American Institute of Physics, New York, 1993) p. 400.
6. C. Benvenuti and M. Hauer, *Supplément à la revue "Le Vide, les couches minces"*, 1981, 201, 199.
7. C. Benvenuti and P. Chiggiato, *Vacuum*, 1993, 44, 511.
8. C. Benvenuti, A. Escudeiro Santana and V. Ruzinov, Proceedings of EVC-6, Lyon 1999.
9. H.F. Winters and E. Kay, *J. of Appl. Phys.*, 1967, 38 (10), 3928.
10. C. Benvenuti, S. Calatroni, P. Chiggiato, M. Marino and R. Russo, Proceedings of the 7th Workshop on Rf superconductivity, Gif-sur-Yvette, 1995, p. 473.
11. S. Amorosi, M. Anderle, C. Benvenuti, S. Calatroni, P. Chiggiato and W. Vollenberg, Proceedings of EVC-6, Lyon 1999.
12. O. Gröbner, A.G. Mathewson, P. Strubin, E. Alge and R. Souchet, *J. Vac. Sci. Technol*., 1989, A 7 (2), 223.
13. P. Chiggiato and R. Kersevan, Proceedings of EVC-6, Lyon 1999.

Figure 1 - Variation of the ultimate pressure, measured in a 58 mm inner diameter chamber, as a function of the baking temperature. The chamber is not vented to air between the baking cycles. Activation begins between 120 and 150 °C and is complete after heating for 24 h at 180 °C.

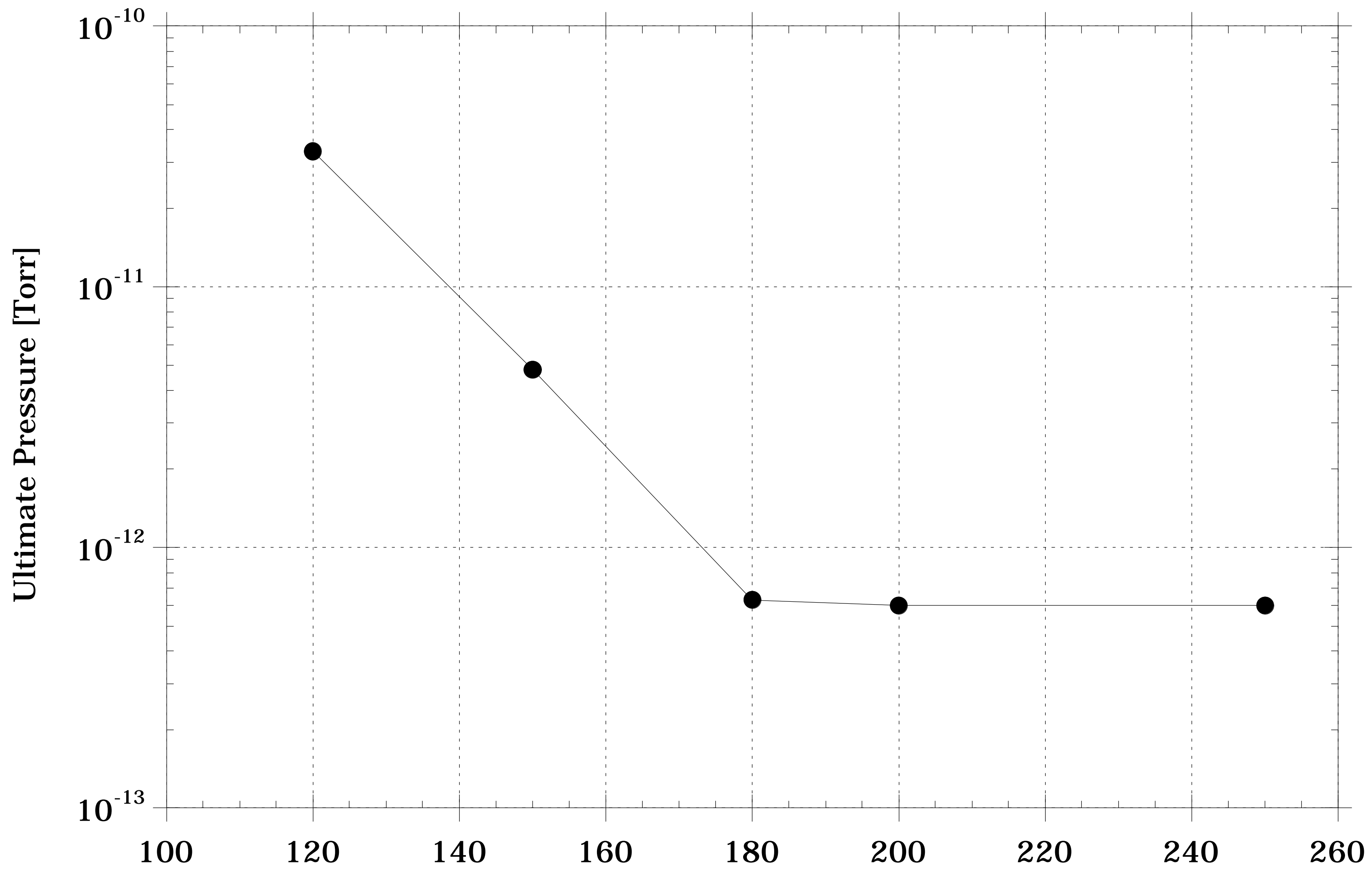


Figure 2 - Quality-composition map of TiZrV thin films produced by means of the three-cathode sputtering system. Two groups of samples are shown, i.e. those providing after 200 °C, 1 hour heating, a Zr metallic to Zr oxide AES peak ratio larger than 0.5 (white dots) and those characterized by a ratio lower than 0.5 (black dots). A large ratio is assumed to be an indication of a more advanced activation. The lower activation temperature is displayed by samples with an amorphous or nanocrystal structure.

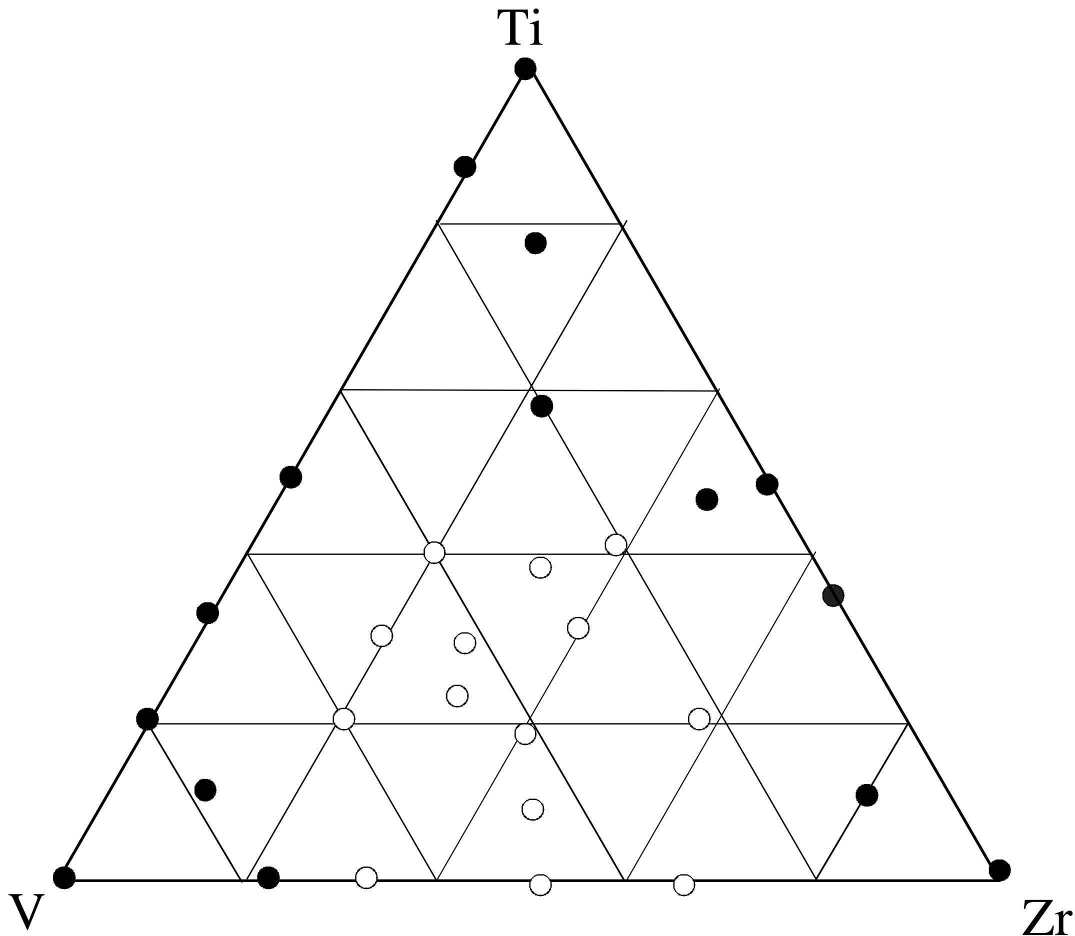


Figure 3 - Variation of pumping speed for CO as a function of the pumped quantity for a TiZrV film (squares) and for a very rough coating (circles). The smooth surface of the TiZrV coating provides a total capacity for CO lower by almost two orders of magnitude. The surface capacity of the rough film is equivalent to that of the ST 707 NEG strip produced by SAES Getters.

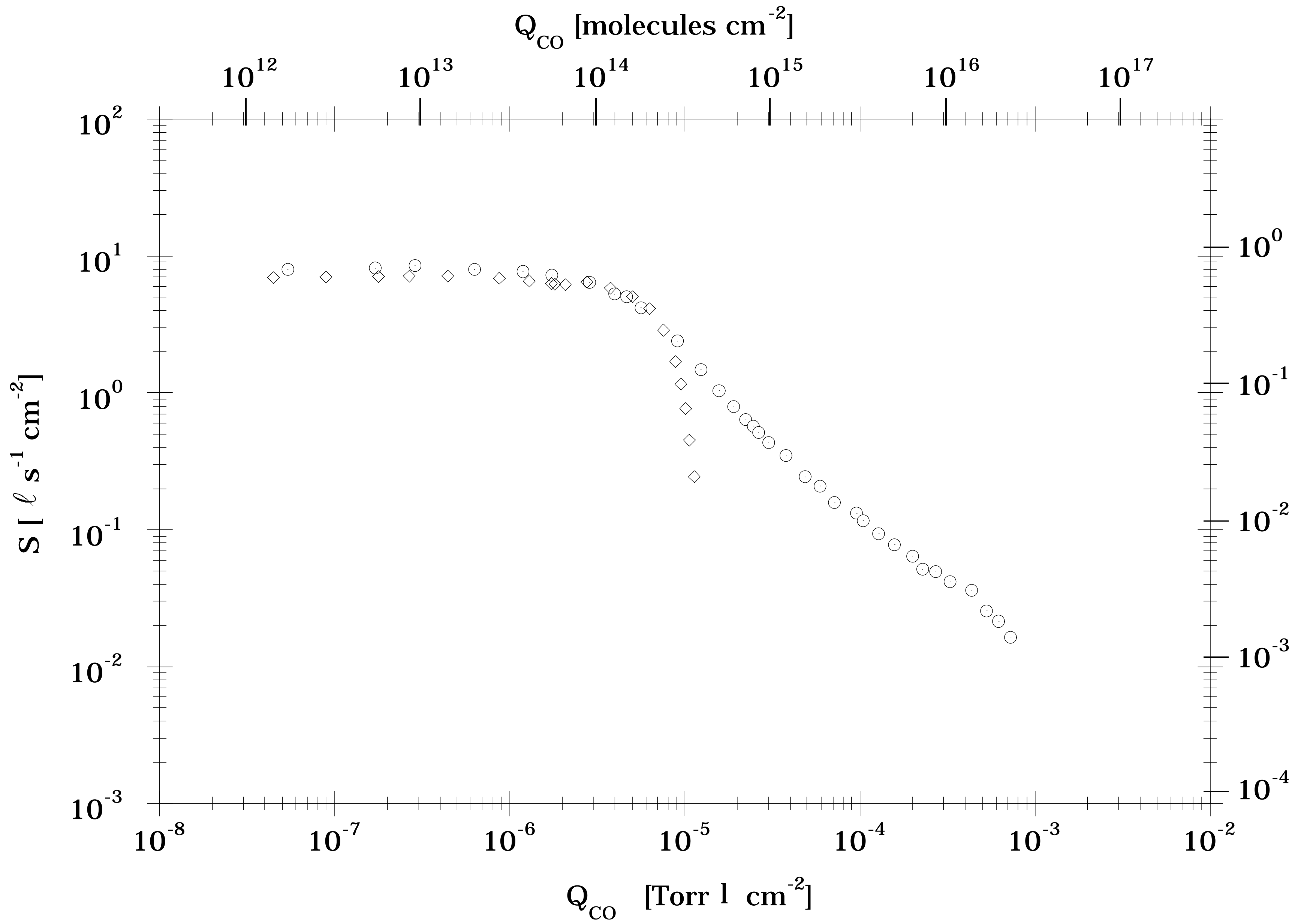
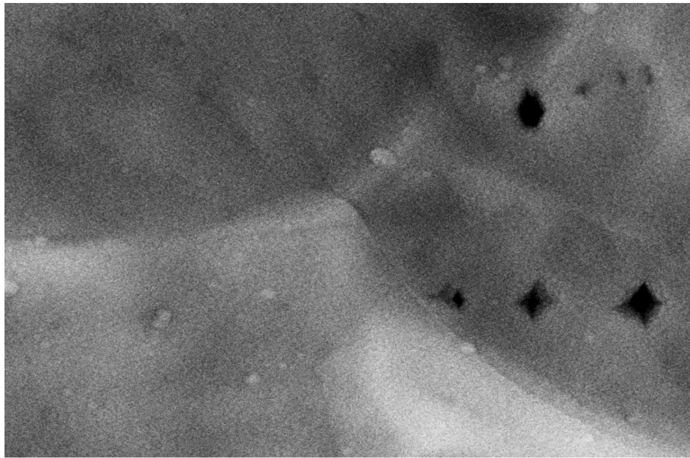
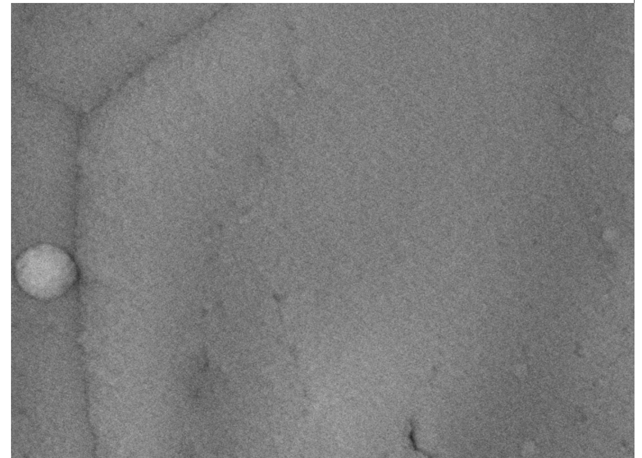
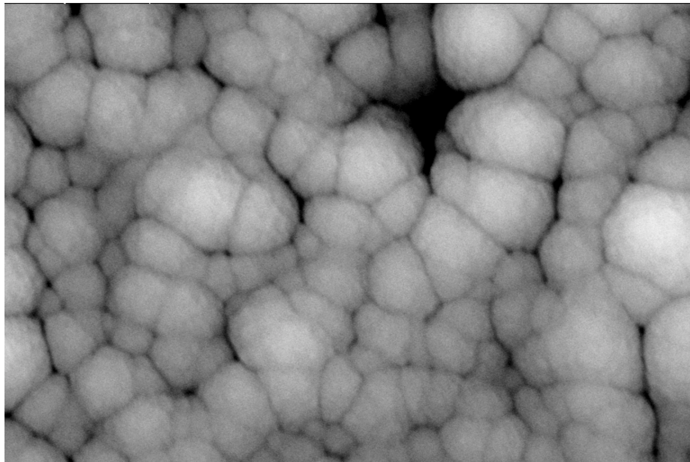

Q_CO [molecules cm^-2]
10^12
10^13
10^14
10^15
10^16
10^17
S [ℓ s^-1 cm^-2]
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^0
10^-1
10^-2
10^-3
10^-4
10^-8
10^-7
10^-6
10^-5
10^-4
10^-3
10^-2
Q_CO [Torr l cm^-2]

Figure 4 - Influence of the nature of the (smooth) substrate on the morphology of TiZrV coatings. The film surface is very smooth when deposited on copper (a) and stainless steel (b), while it displays an appreciable roughness when deposited on aluminium (c) and beryllium (d). Each picture, obtained by Scanning Microscopy, represents a sample surface area of 5 µm x 3 µm







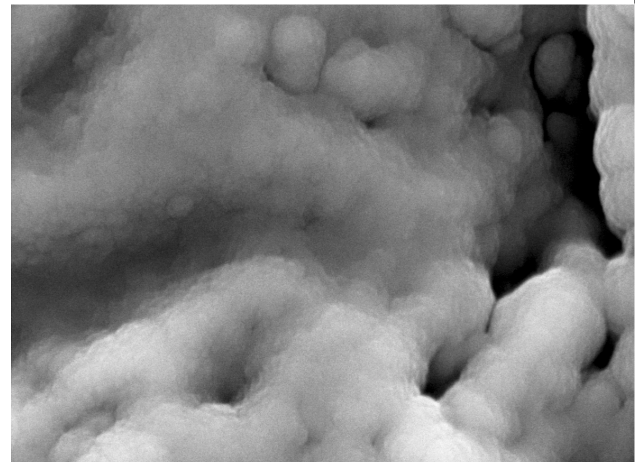


Figure 5 - Variation of the measured ultimate pressures as a function of the H_2 pumping speed provided by the coated chamber at the location of the measuring gauge. The ultimate pressures are measured by the same gauge on 2 m long chambers of different diameter D after different activation procedures. The measuring uncertainty is ± 20 % for gauge sensitivity calibration and $\pm 3 \times 10^{-14}$ Torr for the gauge residual current. The pumping speeds are calculated by a Monte Carlo simulation programme starting from the H_2 sticking factor measured after each bakeout. The full lines represent the upper and lower limits of the contribution due to the gauge degassing.

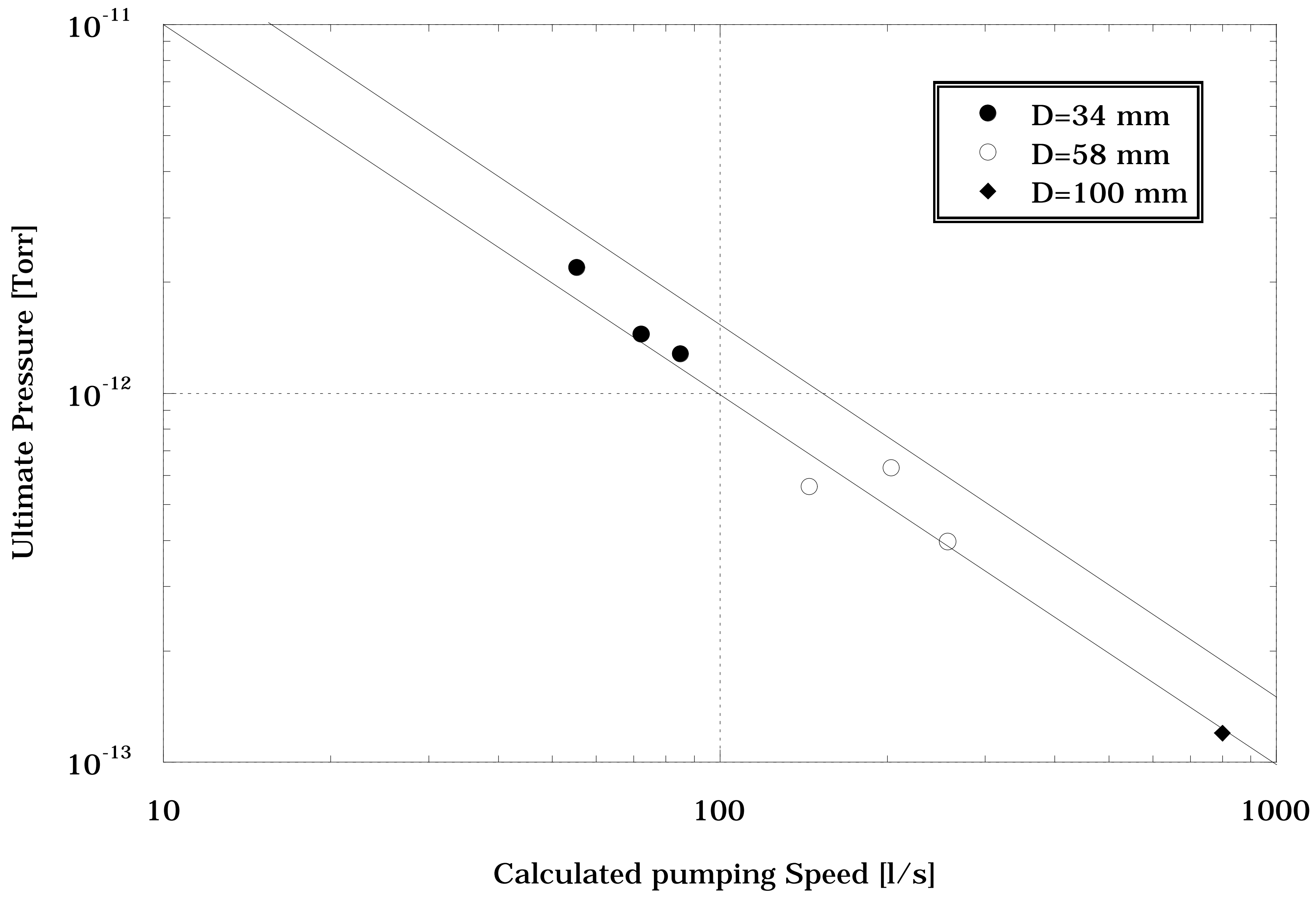


Figure 6 - Variation of the H_2 sticking factor for a 5 μm thick TiZrV film as a function of the number of activation-air venting cycles. The activation temperature applied during 24 h is progressively increased to compensate for the decrease of sticking factor. The figure shows that 26 cycles may be carried out with a 30 % decrease of the H_2 sticking factor provided that the heating temperature is raised to 350 °C.

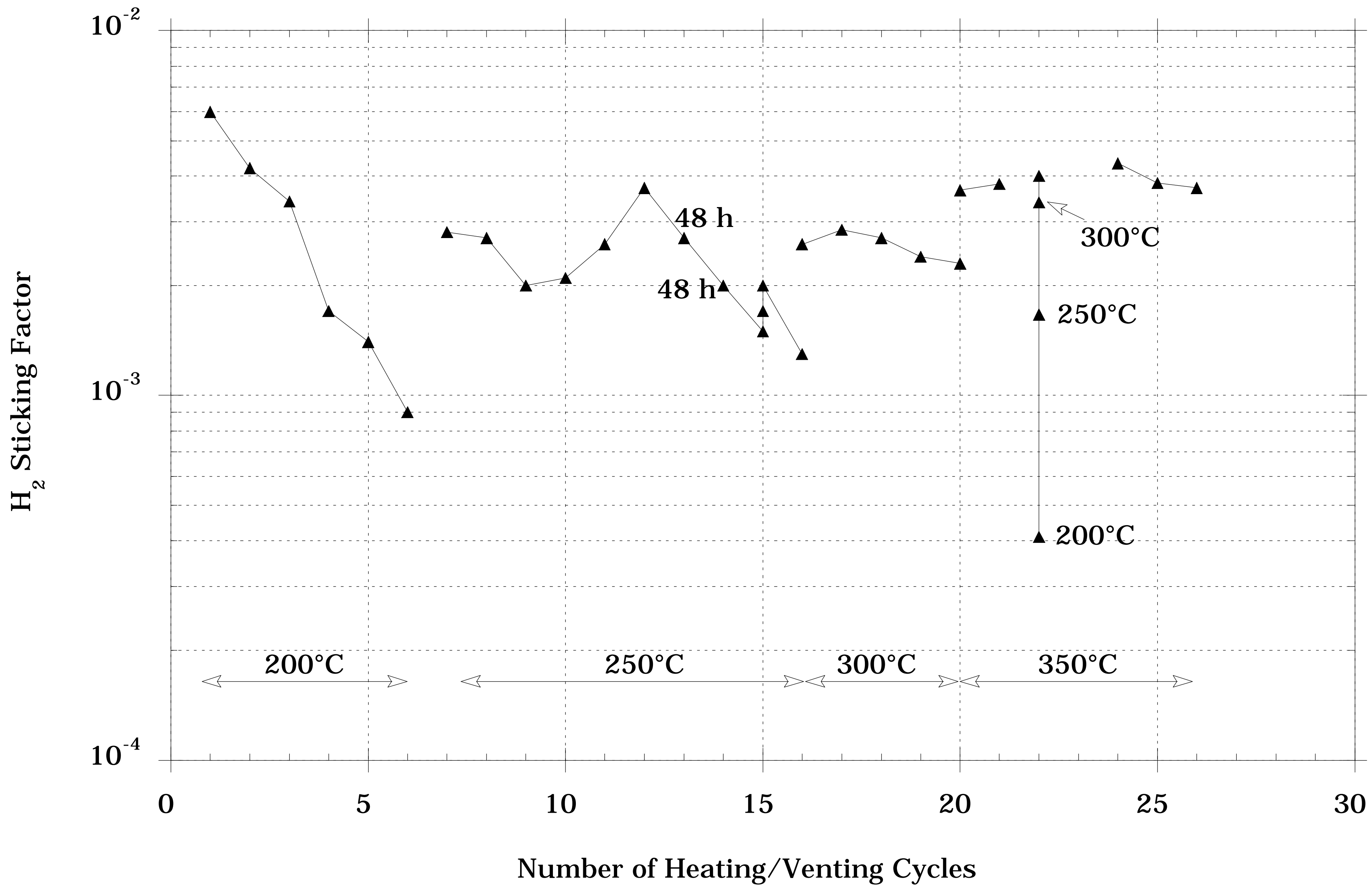


Figure 6 -. Variation of the effective molecular desorption yield as a function of the beam and photon dose measured on a TiZrV coated stainless steel chamber installed on a beam line at ESRF Grenoble. The getter coating activation (250 °C heating for 20 h) is accompanied by a sharp decrease of the desorption yield (about a factor 380), due to both surface cleaning and pumping.