

# Nonevaporable getter films for ultrahigh vacuum applications

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(Received 14 August 1997; accepted 24 October 1997)

The vacuum behavior of stainless steel vacuum chambers, *ex situ* sputter coated with a thin film ( $\sim 1 \mu\text{m}$ ) of getter material, has been studied to determine if after air exposure the getter film could be activated by a bakeout so as to transform the coated vacuum chamber into a pump. The materials studied so far are Ti, Zr, Hf, and some of their binary alloys. They all display an activation temperature lower than 400 °C, i.e., within the reach of the baking temperature of stainless steel vacuum chambers. The lowest activation temperature of 200–250 °C, measured for an equiatomic alloy of Ti and Zr, allows extension of this method to chambers made of copper and aluminum alloys. The experimental results, described here in detail, indicate that the values of the activation temperature obtained using electron stimulated desorption, pumping speed, and Auger spectroscopy measurements are self-consistent. © 1998 American Vacuum Society. [S0734-2101(98)05301-9]

## I. INTRODUCTION

Surface outgassing is the main obstacle to achieving ultrahigh vacuum (UHV) conditions in all-metal vacuum systems. Even after the physisorbed water has been removed by baking, in the presence of surface bombardment by electrons, ions, energetic neutrals, and synchrotron radiation clean metal surfaces are a steady source of gas, namely, H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>.

Since the origin of modern UHV technology, a lot of effort has been devoted to reducing surface degassing by both elaborating on better construction materials and defining sophisticated surface treatments. Many good reviews of the extensive literature on this subject exist and we do not need to expand on it here.

Thin film coatings have been proposed as a way to reduce both thermal and bombardment induced degassing. To fulfill this "passive" function, films of nonreactive materials are considered which are usually produced *ex situ*.<sup>1–4</sup> *In situ* deposition of getter films is common practice in modern vacuum technology to actively pump chemically reactive gases. Many different materials have been proposed and tested, among which the most widely used is certainly titanium, in the form of sublimation pumps. These pumps provide large pumping speeds at low cost, but also produce a very localized pumping action, not suitable for pumping long, conductance limited vacuum chambers as used in large particle accelerators. In this case, a distributed, continuous pumping is preferable, either in the form of an integrated sputter-ion pump<sup>5,6</sup> or of a nonevaporable getter (NEG) strip.<sup>7,8</sup> In both cases the pump is located in a channel parallel to the beam channel, resulting in a design complication and a higher cost of the vacuum chamber. Furthermore, the bombardment induced surface degassing is more effectively pumped but is not reduced.

The ideal solution to the problem would consist in coating *ex situ* the whole vacuum chamber surface with a thin film of NEG material providing a low activation temperature, so as

to allow its activation by *in situ* baking. This NEG film would block the outgassing of the underlying surfaces and would provide, after activation, both a reduced bombardment induced degassing and an additional pumping action.

The availability of industrially produced NEG strips characterized by activation temperatures within the reach of standard baking procedure (i.e., lower than 400 °C) provides evidence that this solution is possible.<sup>9–11</sup> Proof of its existence is given below.

## II. SELECTION OF GETTER MATERIALS

During the activation of a NEG, the surface oxides are dissolved in the material bulk by heating. A low activation temperature implies high oxygen diffusivity in the getter. To cope with the maximum baking temperature allowed by the mechanical properties of construction materials, activation should be feasible at temperatures not higher than 400 °C for stainless steel or never higher than 200 °C for vacuum chambers made of copper or aluminum alloys. On the other hand, the activation temperature should not be lower than 100–150 °C to ensure stability in air at ambient temperature and to avoid water vapor pumping during bakeout. In both cases, the getter film would otherwise be unduly loaded with oxygen and its operating life reduced.

A second important requirement is a high oxygen solubility limit to allow many activation-air exposure cycles. When making the realistic assumption that the thickness of the oxide layer formed during air exposure is 2–3 nm, a 1  $\mu\text{m}$  thick film would present an oxygen concentration of 2%–3% after 10 such cycles. Oxygen concentration could be lowered by increasing the film thickness, but to guarantee a reasonable NEG life a solubility limit in the range of 10% or more is desirable.

As far as H<sub>2</sub> is concerned, to ensure a large pumping capacity at ambient temperature and under UHV conditions the getter should provide high diffusivity, and possibly a hydride phase with low dissociation pressure. Finally, the ideal material should provide large enthalpies of adsorption

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for all the gases which are usually present inside UHV vacuum systems, i.e. H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>.

In addition to these properties which characterize its "vacuum behavior," the selected getter material should also provide other essential features, namely, good adhesion to the substrate, high mechanical resistance, and high melting point (to withstand cathode heating during the coating process; see Sec. III). Furthermore, it should be nontoxic, nonpyrophoric, and if possible inexpensive. Finally, in some cases (e.g., for use in particle accelerators) it should also be nonmagnetic and present a low photoelectric and secondary electron yield to avoid electron emission and multipactoring.

All these requirements are best fulfilled by the elements of the column IV B of the periodic table, i.e., Ti, Zr, or Hf. The most restrictive requirement is the high solubility limit for oxygen, for which only these elements exceed 10%. Therefore, Ti, Zr, Hf, and some of their binary combinations have been taken as an obvious starting point for the present experimental study. However, it should be noted that another family of elements, namely, the rare earths, fulfill most of the requirements listed above, but their study has been postponed because, to the best of our knowledge, their oxygen solubility limit and diffusion coefficient are either inadequate or unknown.<sup>12</sup>

### III. COATING

Sputtering is ideally suited to this application. It is simple, and applicable to a wide range of the materials and alloys, the stoichiometry of which it preserves. It allows uniform and distributed coating of long, narrow vacuum chambers, and can produce alloys/compounds (and also metastable alloys which could not be obtained otherwise) by using composite cathodes. This feature is particularly attractive because elemental materials are easily available, and also because an otherwise pyrophoric coating could safely be produced from stable materials. Once deposited as a thin film, the danger of pyrophoricity is circumvented by the thermal capacity of the substrate, which limits the getter heating which results from exothermic gas absorption.

The samples produced so far are of two distinct types. Those used for vacuum characterization are 50 cm long, 10 cm diameter internally coated stainless steel cylinders. At each coating, small size reference samples on stainless steel, copper, and aluminum alloy are also produced for evaluation of thickness, adhesion, composition, film morphology, and surface analysis.

A magnetron sputtering configuration has been adopted. The cathode consists of a wire (1 mm thick) of the chosen material. Alloys/compounds of variable composition are obtained by twisting together wires of different materials. The required magnetic field is produced by an external solenoid, coaxial to the cylindrical sample. All samples have been produced using the same (nonoptimized) parameters, namely, a magnetic field of  $\sim 100$  G, a cathode voltage of  $-500$  V (sample at ground potential), and an argon pressure of  $2 \times 10^{-2}$  Torr. During coating the cathode reaches a tempera-

ture of  $\sim 1300$  °C and the sample is stabilized at  $100$  °C. The typical deposition rates obtained are of the order of  $1 \text{ \AA s}^{-1}$ .

It is a well established fact that film properties depend strongly on coating parameters. In the present application, for instance, the coating surface roughness, which influences the gas sticking factor and the monolayer surface capacity, is certainly a function of the coating conditions. However, full process optimization is a time consuming activity and provides results valid for a given material only. Therefore, this optimization was postponed until the final material has been selected.

The adopted magnetron sputtering configuration provides a high electron ionization efficiency (the electron path is made longer by the magnetic field), a feature which allows the argon discharge pressure to be reduced, and consequently to limit the energy loss undergone by the sputtered atoms via gas scattering. Since excessive energy loss may endanger film adhesion, this configuration is mandatory whenever the cathode to wall distance is large (10 cm or more). For narrow tubes a simpler diode sputtering configuration would probably be adequate, but this point remains to be investigated.

### IV. CHARACTERIZATION

During NEG activation under UHV conditions, the oxygen surface content is progressively reduced and surface pumping sets in. Activation is completed when the oxygen surface content reaches a minimum and the pumping speed its maximum value. Therefore both surface elemental analysis and pumping speed measurements are adequate means to monitor this activation process. Another possible way consists in measuring surface outgassing induced by electron bombardment [electron stimulated desorption (ESD)], which decreases with decreasing gas surface coverage. Auger spectroscopy, ESD, and pumping speed measurements have been used to characterize the coated samples and the information obtained from these three different methods was found to be self-consistent.

The vacuum system used for simultaneous ESD and pumping speed measurements is shown in Fig. 1. The cylindrical sample is connected at one extremity to a Fischer–Mommson pumping speed measuring dome<sup>13</sup> and at the other extremity to a vacuum system which contains an electron source. The latter may be moved into the sample by compressing long cylindrical bellows. When the sample is to be replaced, the electron source is retracted and protected from air inlet by a gate valve. After installing a new sample, the sample itself and the Fischer–Mommson dome are evacuated, baked to obtain ultimate pressure, then the gate valve is opened, and the electron source inserted inside the sample and operated to measure electron induced degassing. Samples providing low activation temperature are kept at ambient temperature during the first part of the bakeout and heated at  $120$  °C for 2 h at the end of it to minimize the risk of pumping the gases released during bakeout. After bakeout an ultimate pressure in the low  $10^{-10}$  Torr range is typically obtained near the sample when the latter is not activated.

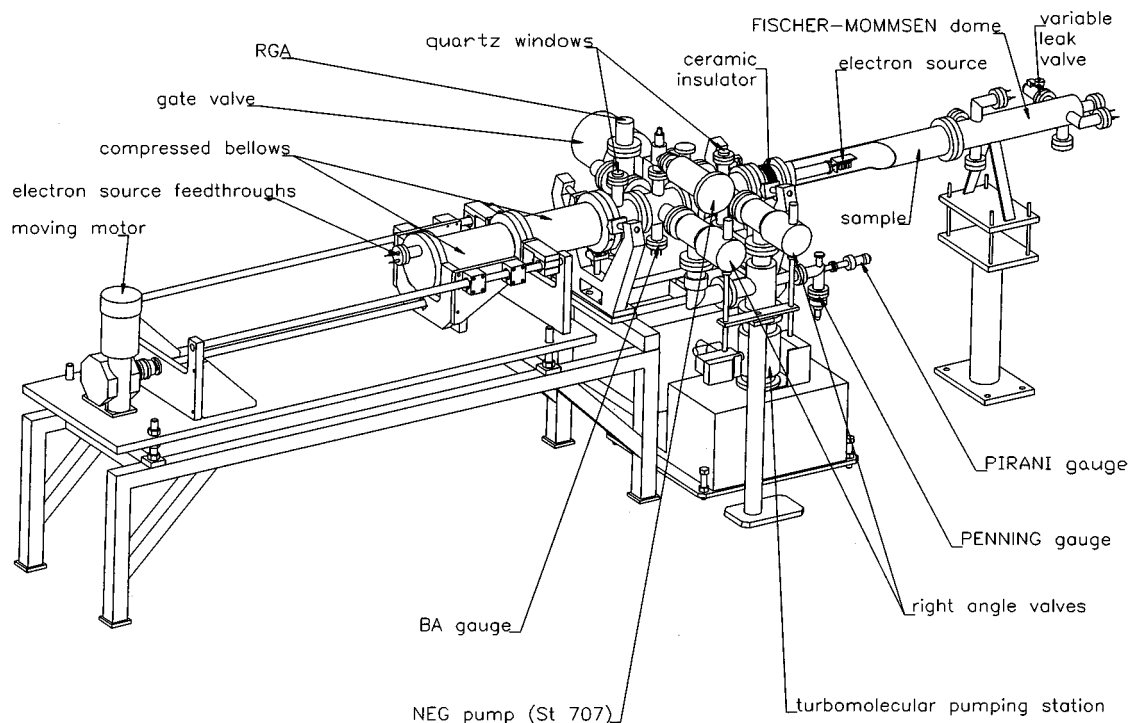


FIG. 1. Schematic view of the vacuum system used for ESD and pumping speed measurements.

After sample activation the ultimate pressure reaches the  $10^{-11}$  Torr range. In both cases,  $H_2$  is the main component of the residual pressure ( $\geq 90\%$ ).

In the standard measuring procedure, the sample is heated for 2 h at a given temperature (starting from  $120^\circ\text{C}$ ), then cooled to ambient temperature before ESD and pumping speed measurements are carried out. This sequence is repeated at intervals of 40 or  $50^\circ\text{C}$  up to a maximum temperature of  $400^\circ\text{C}$ . During sample heating and pumping speed measurements, the electron source is retracted and the gate valve is closed. Pumping is achieved by a turbomolecular pumping station of 240  $\ell/\text{s}$  nominal speed, which is linked to each side of the gate valve by two other valves, so as to allow pumping (with an effective speed of about  $75 \ell/\text{s}^{-1}$  for  $H_2$ ) either side as required. Pressure measurements are carried out by means of three Bayard–Albert gauges (BAGs) and a residual gas analyzer (RGA). The gauges were calibrated against a reference gauge and the accuracy of the reported measurements is  $\pm 15\%$  down to  $10^{-11}$  Torr.<sup>14</sup>

This system has the advantage of providing ESD and pumping speed measurements relative to the same sample conditions. However, it also presents some drawbacks, namely,

- (1) the pumping speed is measured at the entrance of the cylindrical sample. If the sample pumping speed is much larger than the entrance conductance, the system is insensitive to a further surface pumping increase;
- (2) the outgassing species are pumped by the progressively activated surfaces and this effect depends on the position of the electron source in the sample. The larger the

sample length separating the outgassing source from the measuring gauges, the lower will be the measured pressure increase for a given outgassing rate.

To minimize the latter inconvenience, the position of the electron source inside the sample is carefully reproduced ( $150 \pm 1$  mm from the sample extremity where pressure measurements are carried out). However, absolute outgassing information may be obtained only for  $\text{CH}_4$ , which is not pumped by getters. For all other gases, the observed pressure increase is the result of the competing actions of sample outgassing and pumping. Another experimental setup is in preparation, and it will allow measurements to be interpreted in terms of sticking and desorption coefficients by using a more appropriate sample geometry.

During surface bombardment, electron energy and current intensity have been kept constant (500 eV, 1 mA), and the duration of the bombardment at each step short enough to avoid progressive surface cleaning. Also, gas injection for the pumping speed measurement has been minimized in order not to appreciably alter sample surface coverage conditions.

## V. RESULTS

At first, samples coated with elemental Ti, Hf, and Zr were produced and tested. The results are shown in Fig. 2. Titanium follows closely the stainless steel reference curve up to  $300^\circ\text{C}$ , and then quickly drops by two orders of magnitude at  $400^\circ\text{C}$ . Hafnium and zirconium are slightly poorer at the beginning, but activation starts at lower temperatures

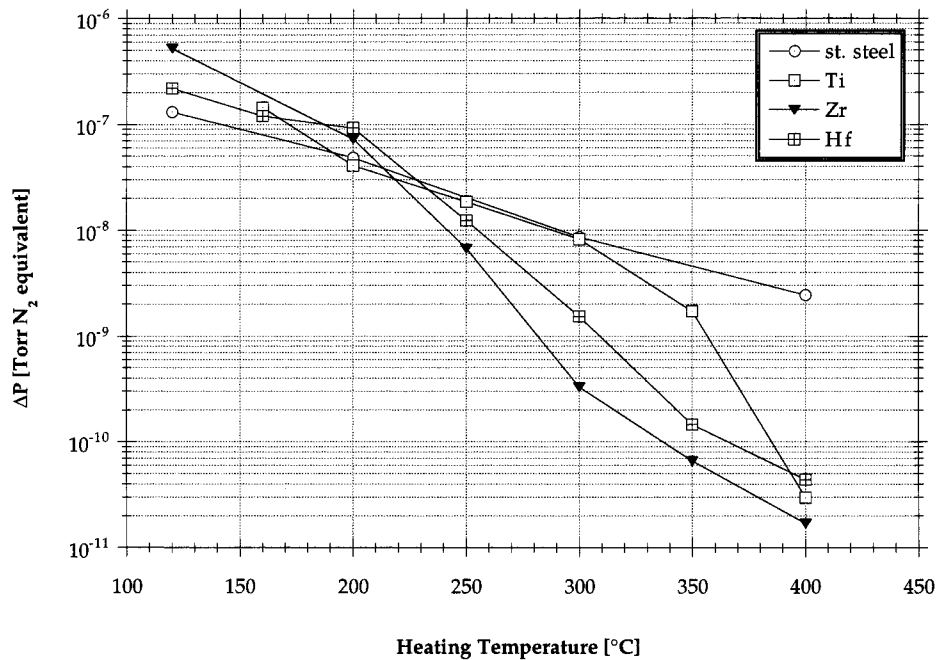


FIG. 2. Total pressure increase induced by electron bombardment of stainless steel and of coatings of Ti, Zr, and Hf. The measurements were carried out at 20 °C after sample heating for 2 h at the indicated temperatures without intermediate air venting. The electron energy was 500 eV and the electron current 1 mA.

(about 200 °C) and sets in more progressively, reaching the same value as titanium at 400 °C. The results of Fig. 2 are a clear indication that these elements are adequate for use on stainless steel chambers, but completely useless when a baking temperature of 200 °C cannot be exceeded, as is the case for chambers made of copper or aluminum alloys.

Many binary combinations of these elements have been explored, but only the results from coatings obtained by combining Ti and Zr will be reported here, because they produced the lowest activation temperature obtained so far. The investigation of other materials, still in progress, will be the object of future publications.

Titanium and zirconium have been combined by using composite cathodes made by one wire of each element or two wires of one element and one of the other. In the following, these samples will be labeled TiZr, Ti(2)Zr, TiZr(2). Their actual composition, measured by energy dispersive x ray (EDX), was found to correspond closely to the macroscopic composition of the cathode.

The results obtained by ESD are shown in Fig. 3. The lowest measured activation temperature corresponds to the TiZr sample. In this case, activation already starts below 150 °C and is practically completed at 300 °C. Two hours at 250 °C are sufficient for an almost complete activation.

The “effective” desorption yields (desorbed molecules per incident electron) for H<sub>2</sub>, CO, CO<sub>2</sub>, and the real desorption yield for CH<sub>4</sub> are shown in Fig. 4 for the same heating cycle. Note the very fast decrease of CO<sub>2</sub> and the leading presence of H<sub>2</sub> at all temperatures. The other samples with different composition also display similar behavior.

The Auger spectra obtained from a TiZr sample when

applying this same heating cycle (2 h at the indicated temperatures) confirm the fast decrease of surface oxygen content between 200 and 350 °C. Further heating to higher temperatures does not change the issue noticeably.<sup>15</sup>

The variation of pumping speed as a function of the heating temperature is shown in Fig. 5. The onset of pumping for CO is evident at about 200 °C, while for H<sub>2</sub> it is shifted to about 250 °C. Taking the sample surface into account (about 1500 cm<sup>2</sup>), and considering only values well below that of the conductance of the tube entrance aperture (about 1000 l/s<sup>1</sup> for CO) the pumping speed for H<sub>2</sub> as observed at the sample tube entrance after heating at 300 °C is approximately 0.3 l/s cm<sup>2</sup>, while this value is already reached for CO at 250 °C. More meaningful pumping speed measurements for pure gases and gas mixtures will be repeated by using a more adequate measuring system (see Sec. IV). After full activation, surface saturation capacities for CO up to the 10<sup>15</sup> molecules cm<sup>-2</sup> range have been measured.

All these results obtained from TiZr samples have been reproduced with minor variations but at slightly higher temperatures when using TiZr(2) and Ti(2)Zr. The emerging global picture provides overwhelming evidence that TiZr is the most adequate composition for applications where the heating temperature must be reduced to a minimum. This conclusion agrees with results reported in the literature,<sup>16,17</sup> obtained by measuring the weight increase while heating samples of different Ti and Zr content in air at 700 °C. In this case, the rate of the weight increase presents a maximum corresponding to equal atomic concentrations of these two elements, showing that this composition provides the highest oxygen diffusion coefficient.

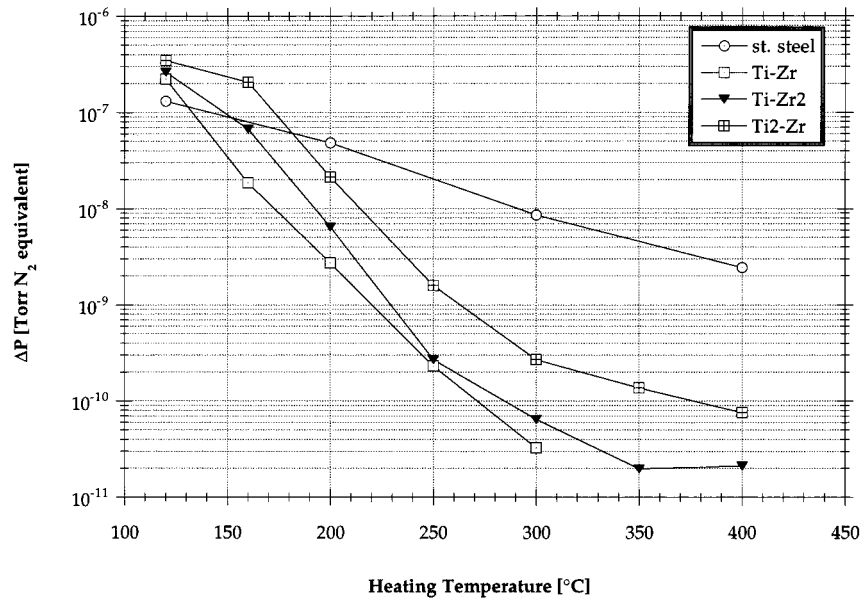


FIG. 3. The same as in Fig. 2 but for TiZr alloys of different compositions.

A legitimate question to be asked is how much a reduced heating temperature may be compensated for by an increased heating duration. The answer is given in Fig. 6. In this figure, the dashed area represents the spread of the results from five different TiZr samples subjected to the standard 2 h heating cycle and the experimental points represent the results obtained by extended 150 °C heating at first and 200 °C heating afterwards. The results at 200 °C have been reproduced also by venting the same sample to air and skipping the 150 °C step. The practical conclusion, which may be derived from

these data, is that 24 h both at 150 and 200 °C provides an ESD performance similar to that obtained when heating for 2 h at a temperature 50 °C higher.

A further important feature concerns performance deterioration consequent to the accumulation of activation-air venting cycles (aging). The ESD results obtained for five such cycles are shown in Fig. 7. The conclusion is that the ESD performance of a 1.5 μm thick TiZr coating is marginally affected by five cycles. Even minor deterioration may be expected for thicker coatings. Another possible cause of de-

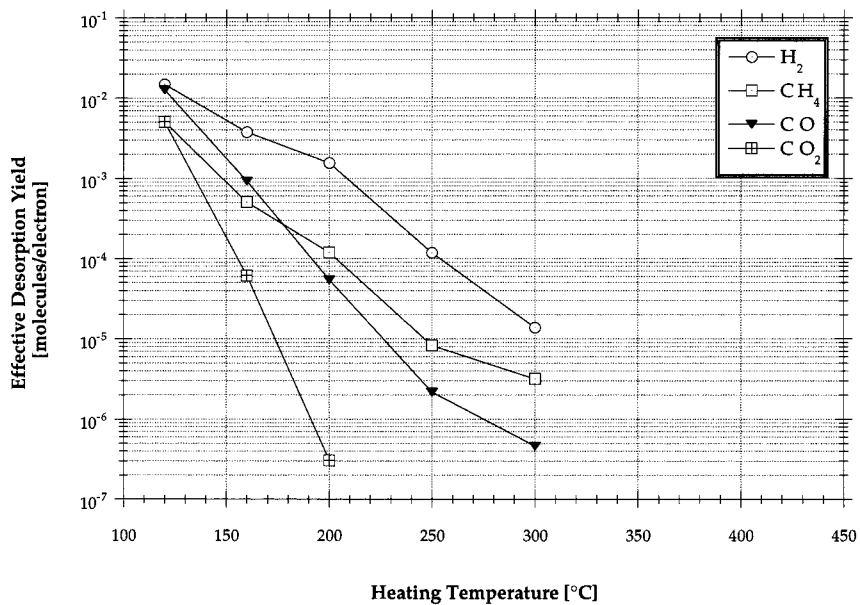


FIG. 4. Effective desorption yield of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> for an equiatomic TiZr coating. The measuring conditions are the same as those indicated for Fig. 2. “Effective” here indicates the net desorption per impinging electron as determined by the particular experiment geometry.

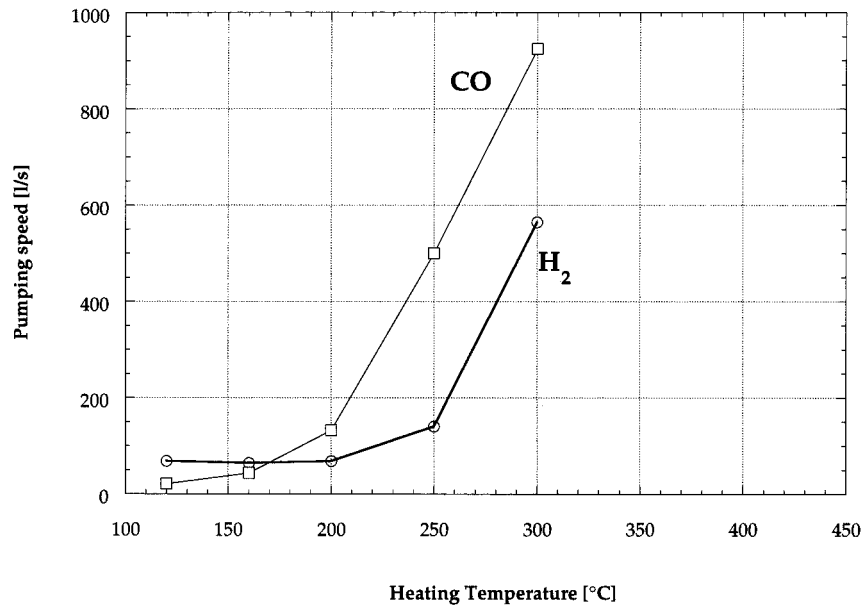


FIG. 5. Pumping speed variation as a function of the heating temperature for H<sub>2</sub> and CO of a TiZr coated sample. The measurements were carried out at 20 °C after 2 h heating at the temperature indicated.

terioration may be the extended exposure to ambient air. To clarify this point, a sample has been kept in ambient air for 3 months. When remeasured, this sample did not show any appreciable performance decrease.

**IV. CONCLUSION**

Evidence has been obtained that low activation temperature coatings exist. The lowest measured activation temperature, for equiatomic coatings of Ti and Zr thin film, is about

250 °C when heating for 2 h and about 200 °C if heating is extended to 24 h. If baking temperatures up to 400 °C are allowed, a much larger choice of coatings is available.

The TiZr coatings (1.5 μm thick) may be stored in air for months and undergo up to at least five activation/air venting cycles without relevant performance deterioration. Large pumping speeds have been measured together with surface saturation concentrations of up to the 10<sup>15</sup> molecules cm<sup>-2</sup> range. Precise pumping speed and saturation surface cover-

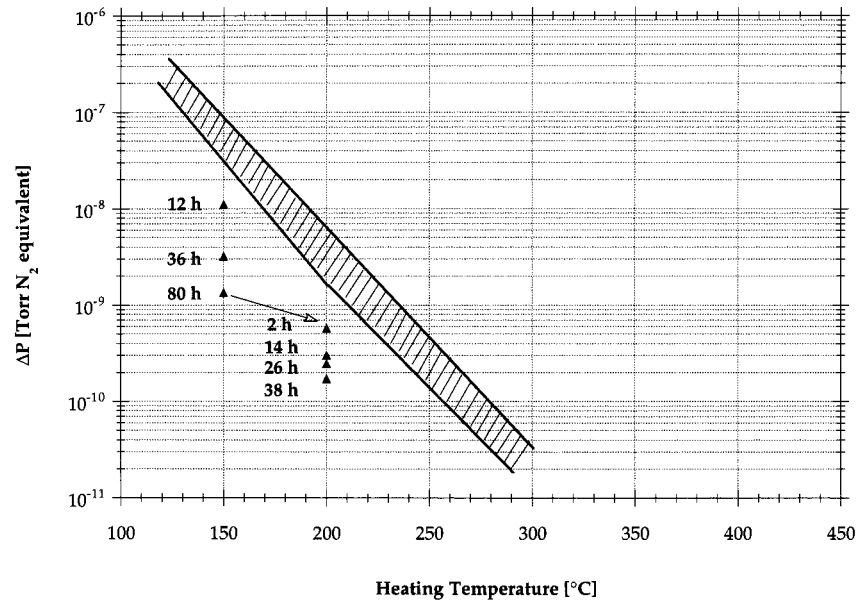


FIG. 6. Variation of the electron stimulated total pressure increase for various durations of the applied sample heating (TiZr coated sample). The dashed area indicates the spread of the results relative to five different samples (2 h heating). The triangles correspond to the measurements carried out at 20 °C after the heating periods indicated.

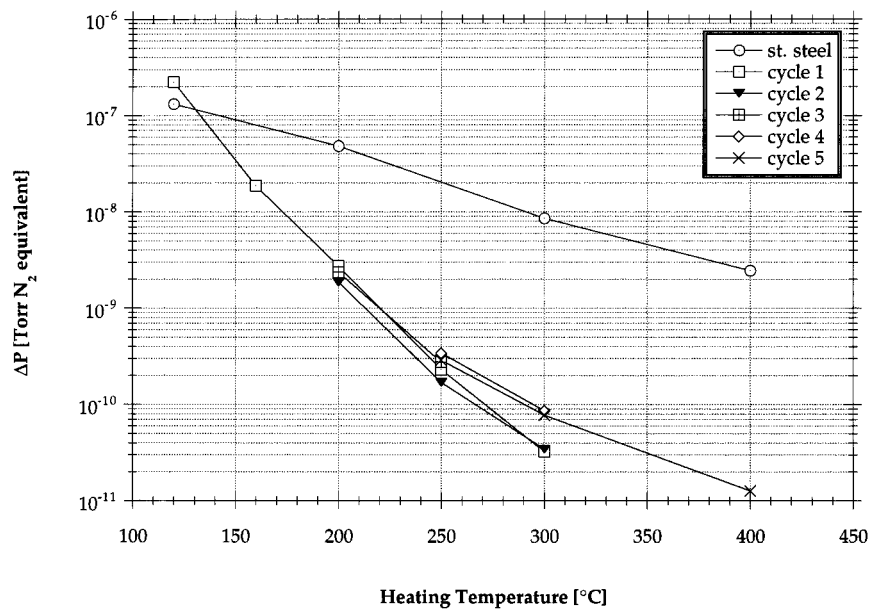


FIG. 7. Variation of the electron stimulated pressure increase for the same TiZr coated sample after five activation-venting cycles.

age measurements will be carried out soon.

The available results do not provide any information with respect to the getter film effectiveness for trapping H<sub>2</sub> originating from the underlying substrate. This effect, which will also be explored soon, should be present even in the absence of getter film activation and might allow unrivaled ultimate pressures to be achieved inside (almost) completely coated vacuum systems.

## ACKNOWLEDGMENTS

The authors are indebted to S. Calatroni for suggesting the sputtering configuration and to J. Fraxedas and M. Hauer for their participation in the designing, commissioning, and first use of the ESD system. The technical assistance of R. Jacob is gratefully acknowledged.

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