



Decreasing surface outgassing by thin film getter coatings

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The UHV behaviour of stainless steel vacuum chambers, coated ex situ by sputtering with a thin film of a getter material, has been investigated. The purpose of this study was to ascertain if the getter film could be activated after air exposure by in situ baking, so as to transform the vacuum chamber from a gas source into a pump.

Many elements and alloys have been tested, all of which could be activated by baking at temperatures acceptable for stainless steel components, i.e. lower than 400°C. In one case (equiatomic TiZr alloy) an activation temperature of 200–250°C has been measured.

This investigation has been carried out using Electron Stimulated Desorption, pumping speed and ultimate pressure measurements. © 1998 Elsevier Science Ltd. All rights reserved

Introduction

Surface outgassing is the main obstacle to achieving extreme vacua. Even after vacuum firing at 950°C and *in situ* baking at 300°C, stainless steel vacuum chambers outgas H₂ at a rate of about 10⁻¹³ Torr s⁻¹ cm⁻², so requiring pumping speeds higher than 10³ l s⁻¹ per square meter of chamber surface to obtain ultimate pressures lower than 10⁻¹² Torr.¹

In the case of particle accelerators making use of small aperture vacuum chambers, the problem is aggravated by the reduced pumping conductance and by the degassing consequent to surface bombardment by photons, electrons and ions. To circumvent these obstacles, linearly distributed pumping is usually adopted, either in the form of integrated sputter-ion pump² or of a Non Evaporable Getter (NEG) strip.³

An even better solution would consist in sputter-coating the vacuum chamber with a thin getter film to be activated *in situ* bakeout. In this case not only linear pumping would be achieved without requiring any additional space, but also the underlying chamber outgassing would be inhibited and the bombardment induced surface degassing strongly reduced. The purpose of the present study was to investigate the feasibility of this solution.

Choice of the getter material

The getter materials potentially interesting for this application should provide high binding energies for reactive gases, high

absorption capacity and low dissociation pressure for hydrogen, high diffusivity for oxygen to allow low temperature activation, and high oxygen solubility to accommodate the uptake of this gas consequent to many activation-air venting cycles. All these requirements are fulfilled by the elements of the IV B column of the periodic table, namely Ti, Zr, Hf. Therefore, this study has been focused on these elements and their binary combinations.⁴

Coating and characterization systems

Chamber coating is carried out in the magnetron sputtering configuration (discharge voltage 500 V, argon pressure 2 × 10⁻² Torr, deposition rate ~1 Å/s, magnetic field ~100 G). The magnetic field is provided by an external solenoid coaxial to the chamber. The cathode is a wire (1 mm diameter) stretched along the chamber axis. Composite cathodes obtained by intertwining wires of different elements are used to produce (usually) binary alloys. The coating thickness is standardised to 1.5 μm.⁴

The coated chambers are characterised by means of two different vacuum systems, one of which dedicated to Electron Stimulated Desorption (ESD) and pumping speed and the other one to ultimate pressure measurements. In this first system, shown in Fig. 1, a 50 cm long, 10 cm diameter, coated chamber is linked at one extremity to a Fischer-Mommsen measuring dome and at the other extremity to a vacuum system containing the electron source, usually isolated by a gate valve.⁴ By opening this valve and compressing long bellows, the electron source may be brought inside the coated chamber and surface electron bombardment carried out. The electron energy has been standardised at 500 eV and the electron current intensity at 1 mA. During pumping speed measurements the electron source is retracted and the gate valve

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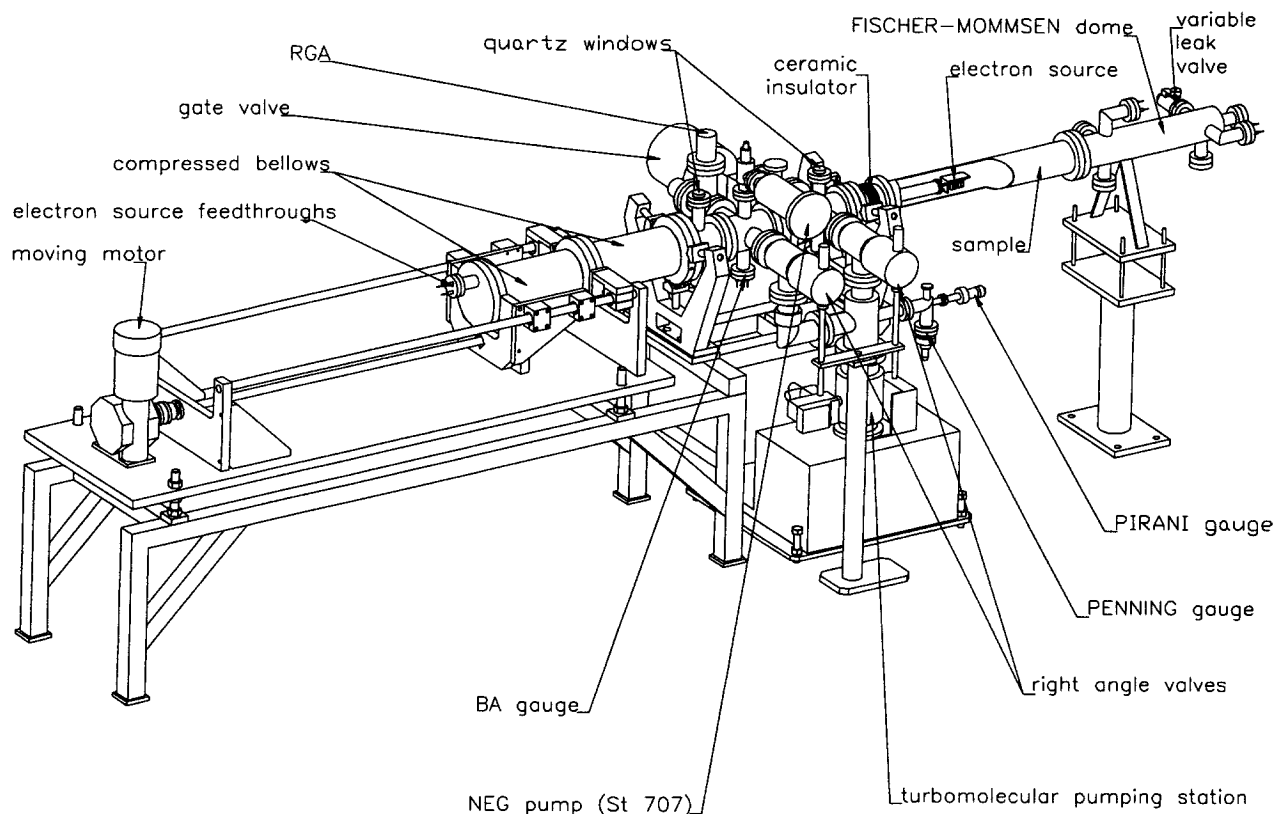


Figure 1. Schematic view of the vacuum system used for ESD and Pumping Speed measurements.

closed. During all measurements the system is pumped by a turbomolecular pump providing an effective pumping speed of about 75 l s^{-1} for H_2 .

For ultimate pressure measurements, two chambers 1 m long, 16 cm diameter, providing a total coated surface area of about 1 m^2 , are linked together and connected to a pumping system via an orifice of 25 l s^{-1} conductance for H_2 . The pumping system, equipped with turbomolecular, sputter-ion and titanium sublimation (nitrogen cooled) pumps, is capable of an ultimate pressure lower than 10^{-12} Torr. At the free extremity of the coated chambers the pressure is monitored by means of an improved Helmer type gauge, able to measure pressures down to the 10^{-14} Torr range.⁵

Results

Pumping speed and ESD measurements have been carried out on chambers coated with Ti, Zr, Hf and some of their alloys. The results obtained on elemental coatings are shown in Fig. 2 together with those relative to a stainless steel vacuum chamber vacuum fired at 950°C .⁴

Titanium follows closely the stainless steel reference curve up to 300°C , and then quickly drops by two orders of magnitude at 400°C . Hafnium and zirconium are slightly worse at the beginning, but activation starts at lower temperatures (about 200°C) and sets in more progressively, to reach 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 made of copper or aluminium alloys.

The results obtained on equiatomic binary Ti, Zr, Hf alloys (produced by means of composite cathodes made by intertwining two wires of different materials) are shown in Fig. 3. The alloys display a lower activation temperature compared to elemental coatings, and the lowest activation temperature corresponds to TiZr. In this case activation starts below 150°C and is practically completed at 300°C . Two hours at 250°C are sufficient for an almost complete activation.

Since Ti and Zr mixing provides the lowest activation temperature, the composition of the TiZr alloy has been varied by using cathodes obtained by intertwining two wires of one element and one of the other. The results, shown in Fig. 4, indicating that the equiatomic TiZr alloy still provides the lowest activation temperature,⁴ and that consequently it is the most adequate for applications where the heating temperature must be reduced to a minimum. This conclusion agrees with results, reported in literature,^{6,7} obtained by measuring the weight increase while heating samples of different Ti and Zr content in air at 700°C . In this case, 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.

The "effective" desorption yields (desorbed molecules per incident electron) for H_2 , CO , CO_2 and the real CH_4 desorption yield for the equiatomic TiZr alloy are shown in Fig. 5.⁴ Note the very fast decrease of CO_2 and the leading presence of H_2 at all temperatures. All the other samples with different composition also display a similar behaviour.

The variation of pumping speed as a function of the heating

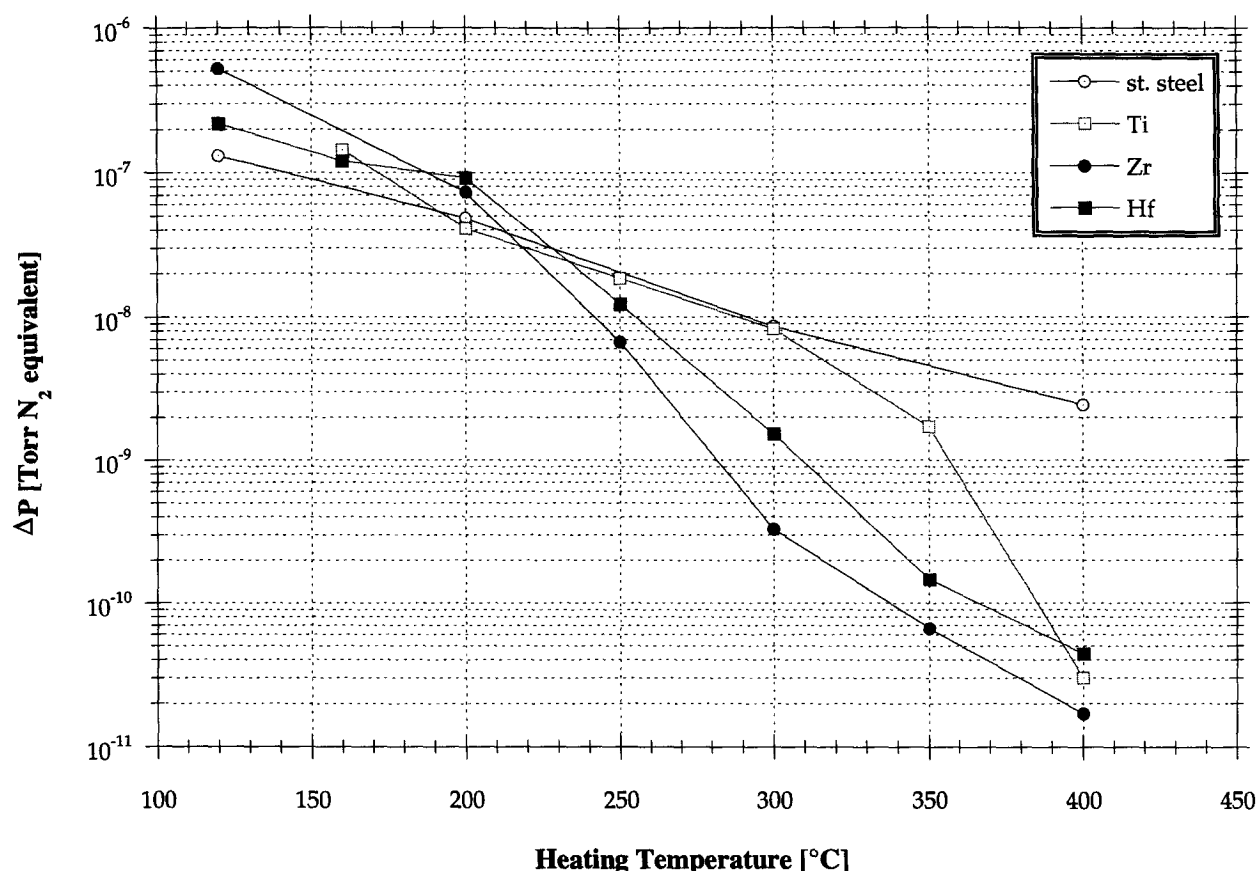


Figure 2. Total pressure increase induced by electron bombardment of stainless steel and of coatings Ti, Zr, Hf. The measurements are carried out at 20°C after sample heating for 2 h at the indicated temperatures. The electron energy is 500 eV and the electron current 1 mA.

temperature is shown in Fig. 6.⁴ The onset of pumping for CO is evident at about 200°C, while for H₂ it is shifted to about 250°C. Taking the sample surface into account (about 1500 cm²), and considering only values far from the conductance of the tube entrance aperture (about 1000 l s⁻¹ for CO), the pumping speed for H₂ after heating at 300°C is of the order of 0.3 l s⁻¹ cm⁻², while this value is already reached for CO at 250°C. More precise pumping speed measurements for pure gases and gas mixtures will be repeated by using a more adequate measuring system. After full activation, surface saturation capacities for CO up to the 10¹⁵ molecules cm⁻² range have been measured.

A legitimate question to be asked is how much a reduced heating temperature may be compensated for by increasing heating duration. The experimental evidence⁴ indicates that 24 h heating at a given temperature provides the same ESD performance as obtained when heating for 2 h at a temperature about 50°C higher. A further important feature concerns performance deterioration consequent to the accumulation of activation-air venting cycles (ageing). The ESD results obtained for five such cycles indicate that the ESD performance of 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 deterioration may be the extended exposure to ambient air. To clarify this point, a sample has been kept in ambient air for three months. When measured, this sample did not show any

appreciable performance decrease⁴ compared to newly coated samples.

The ultimate pressures obtained on TiZr coated tubes are shown in Fig. 7. These pressures have been reached after 24 h baking at the temperatures indicated on the abscissa, starting from 150°C and increasing the temperature in steps of 50°C without intermediate air venting. As Fig. 7 shows, a pressure in the low 10⁻¹³ Torr range has been achieved after 200°C baking, while baking above 250°C results in ultimate pressure in the 10⁻¹⁴ Torr range, i.e. similar to what obtained by using NEG strips.⁸ Partial pressures could not be quoted because adding the residual gas analyzer and the related (uncoated) connecting manifold resulted in an increased gas load which limited the ultimate pressure to the 10⁻¹² Torr range.

After each baking step, H₂ and CO have been injected on the pumping system, before the conductance orifice, while the pressures were measured both at injection side and at the other end of the coated tubes. In order to extract from these pressures an approximate value of the pumping speed, their ratio is multiplied by the orifice conductance (25 l s⁻¹ for H₂). The results, shown in Fig. 8, indicate that pumping speeds of the order of 0.1 l s⁻¹ cm⁻² may be obtained after 200°C bakeout for CO and 250°C bakeout for H₂, while a value of about 1 l s⁻¹ cm⁻² for both gases is obtained after baking at 350°C.

It is worth noting that after 150°C baking there is no surface

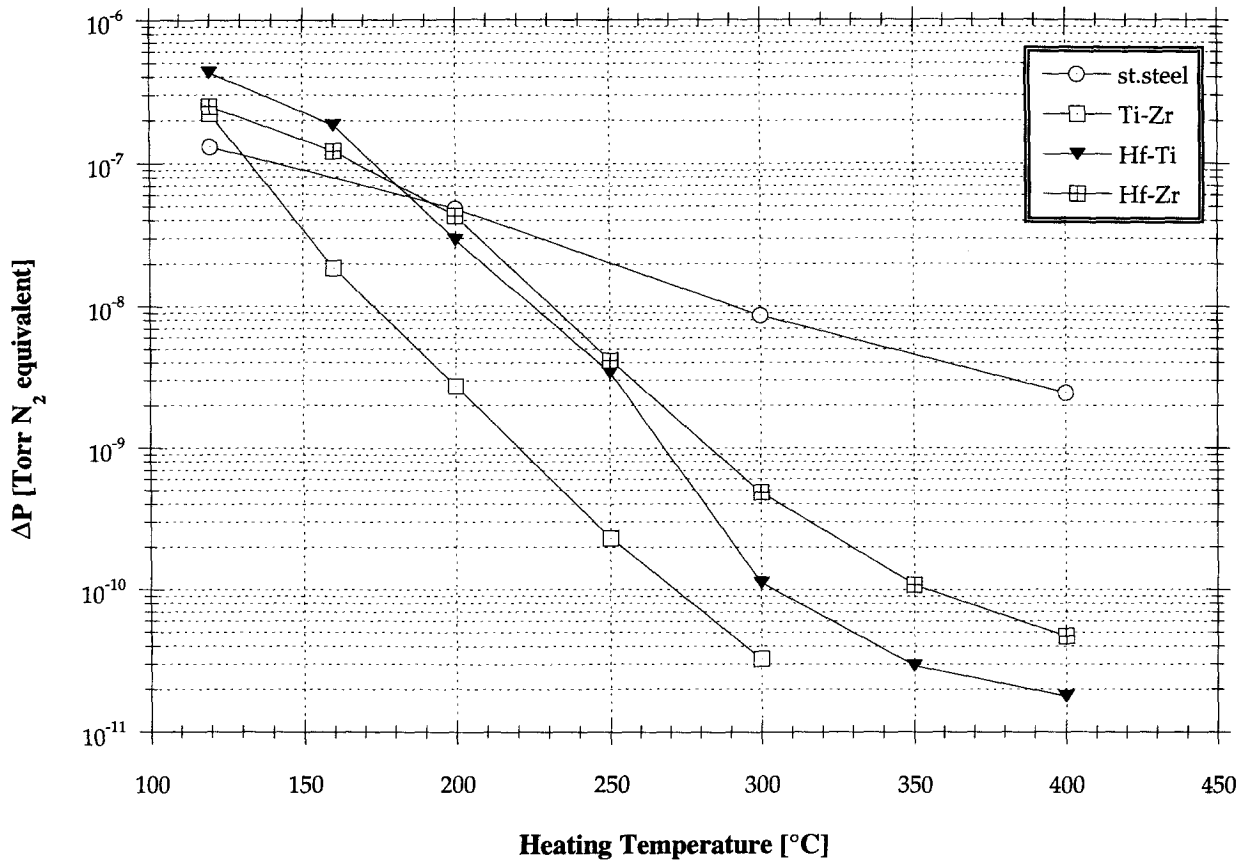


Figure 3. Same as Fig. 2, for binary equitatomic alloys of Ti, Zr, Hf.

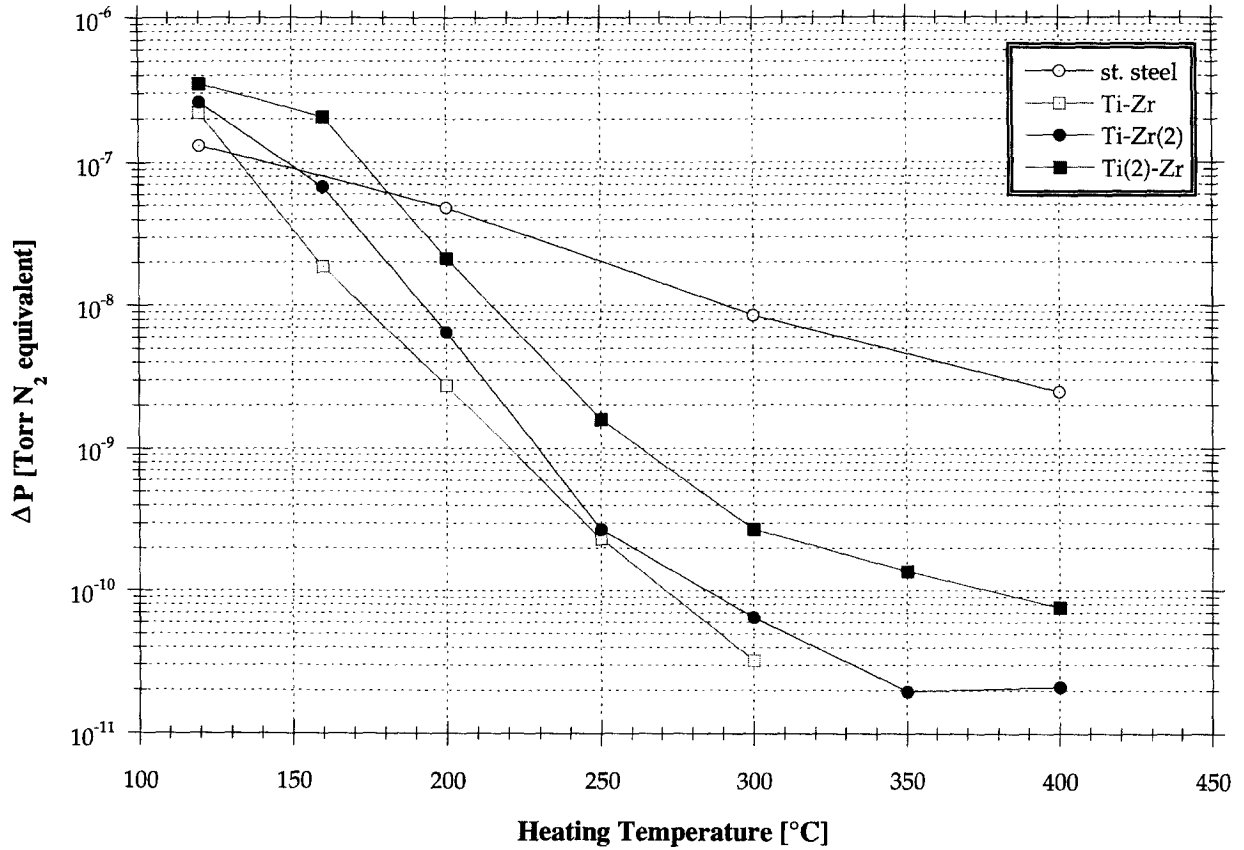


Figure 4. Same as Fig. 2 for TiZr alloys of different composition.

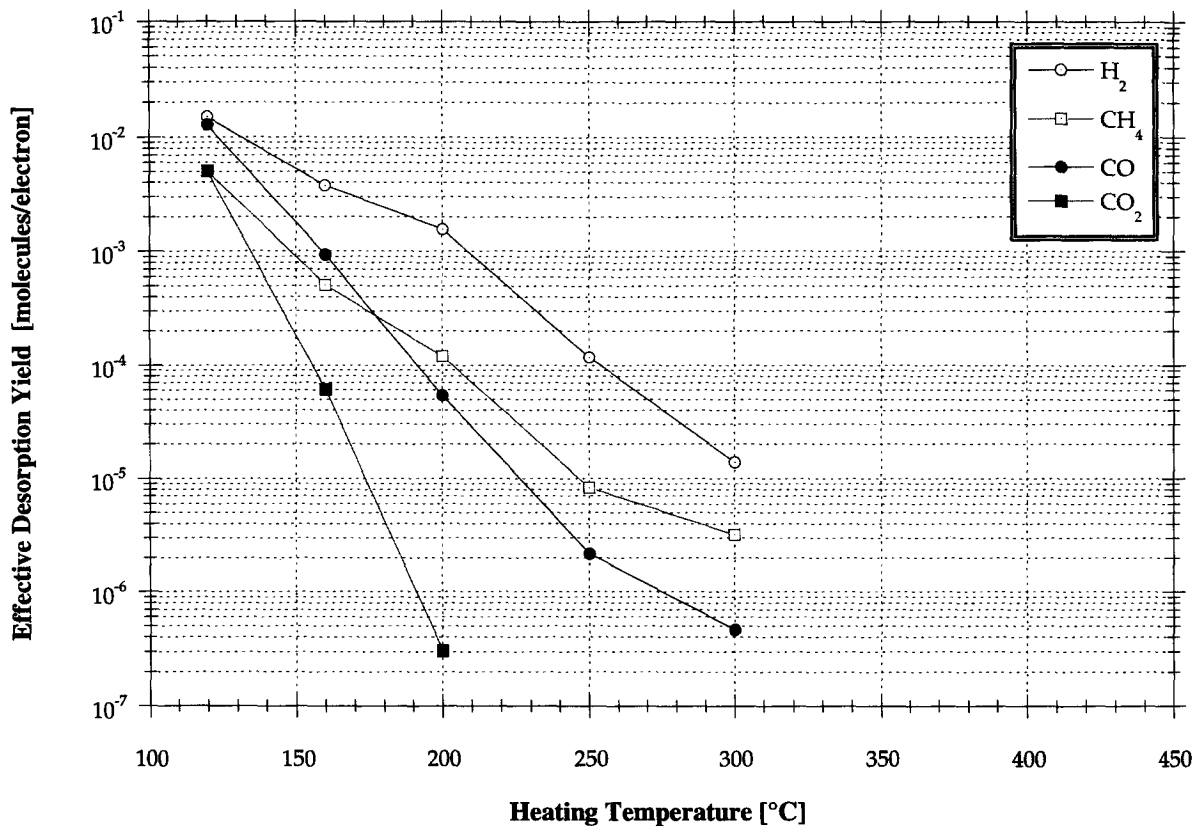


Figure 5. Effective desorption yield of H₂, CO, CO₂ and CH₄ for an equiatomic TiZr coating. The measuring conditions are the same as indicated for Fig. 2. “Effective” here indicates the net desorption per impinging electron, as resulting from the competing action of surface degassing and pumping. Since CH₄ is not pumped, the measurements represent a real desorption yield for this gas.

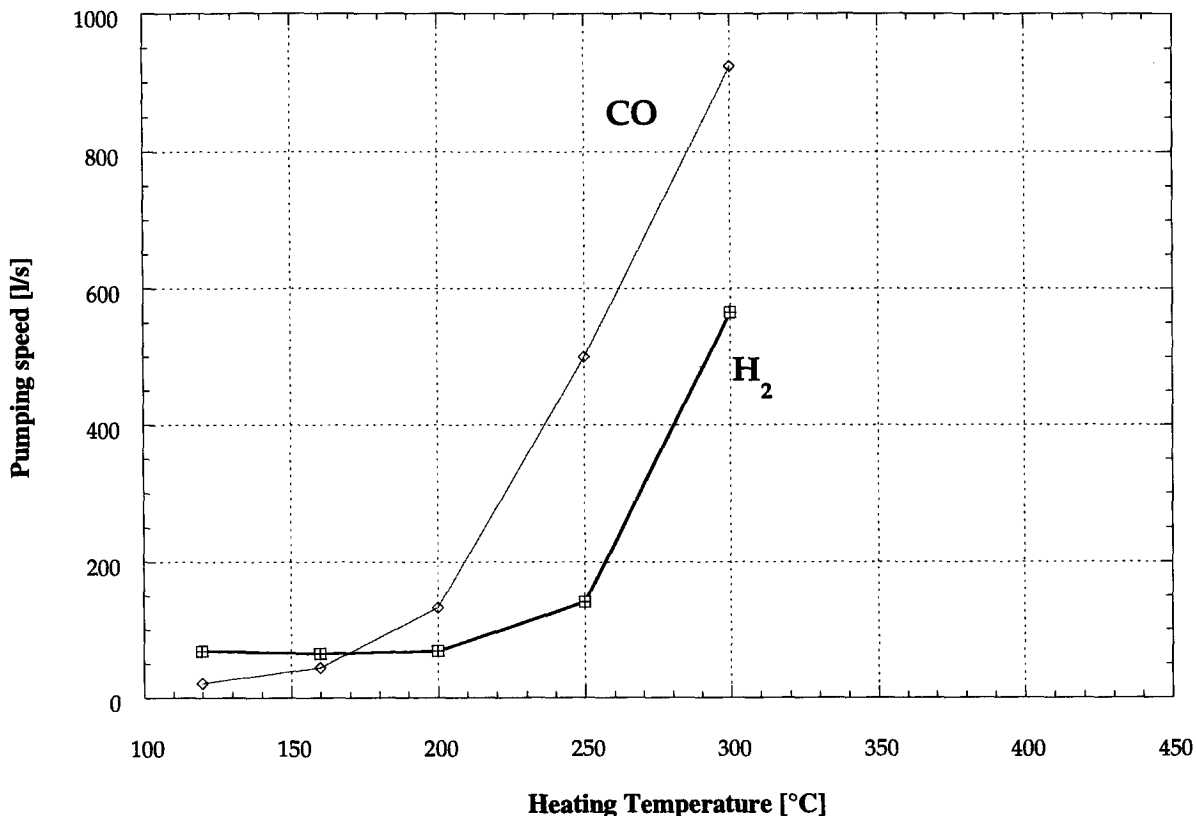


Figure 6. Pumping speed variation as a function of the heating temperature for H₂ and CO of a TiZr coated sample. The measurements are carried out at 20°C after 2 h heating at the indicated temperature.

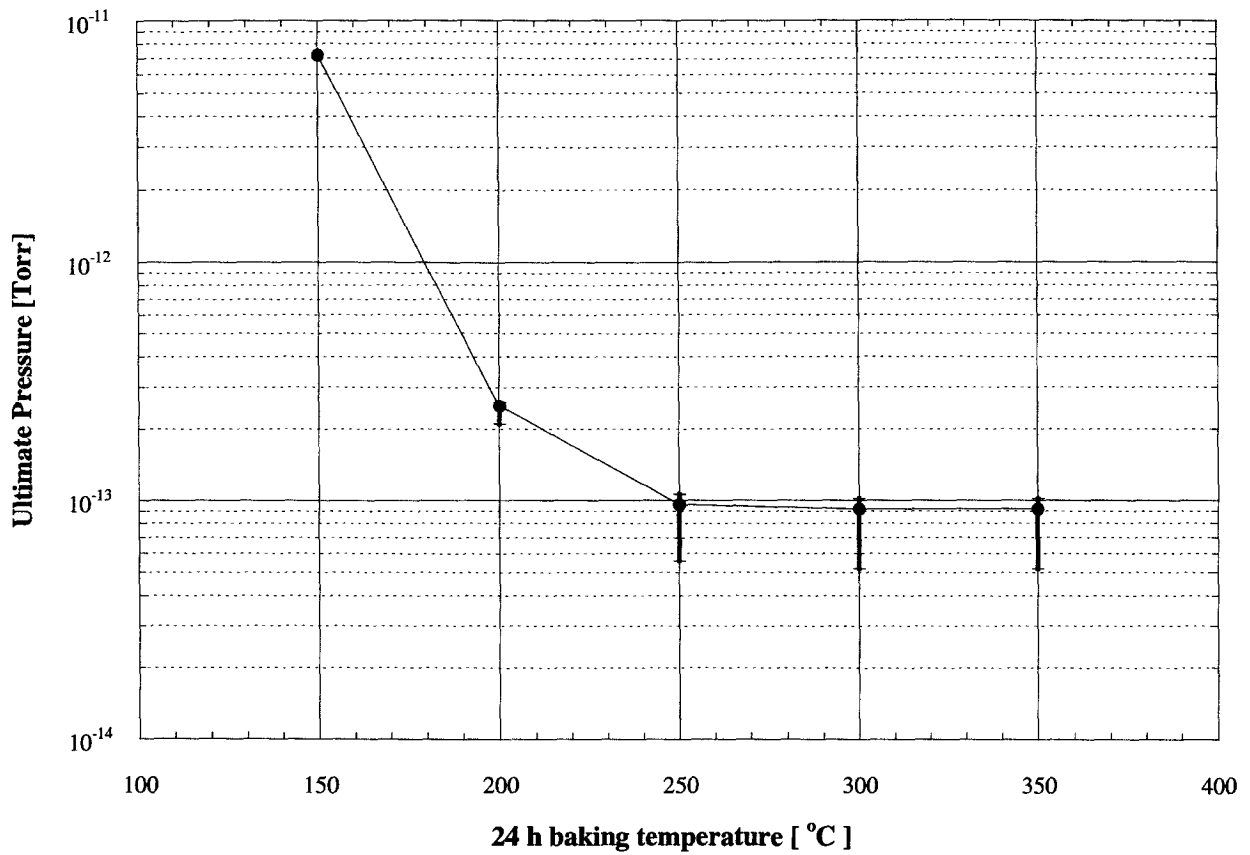


Figure 7. Ultimate pressure achieved on the 2 m long TiZr coated chambers after 24 h baking at the indicated temperatures.

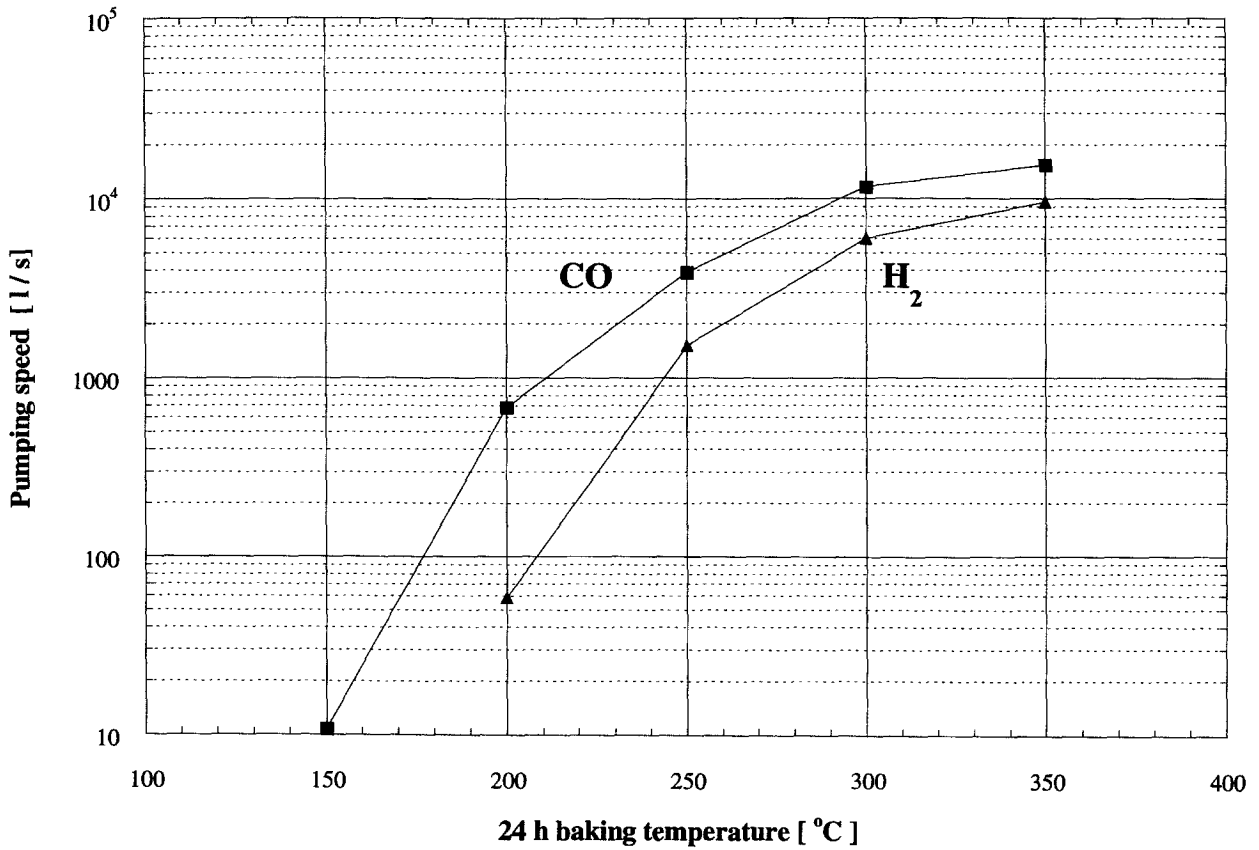


Figure 8. Pumping speed values obtained after 24 h baking at the indicated temperatures for the 2 m long TiZr coated chambers.

pumping and therefore the measured ultimate pressure and the orifice conductance allow calculating a specific H₂ outgassing rate of 5×10^{-14} Torr l s⁻¹ cm⁻² when assuming that only H₂ is present. A more precise estimate of this quantity would require knowing the gas composition, which unfortunately is not available for the reasons mentioned above. Therefore, the quoted value should be considered an upper limit only. Gases such as CH₄ and Ar, not pumped by the getter coating, provide a higher gauge sensitivity and a lower conductance than H₂, and they may heavily affect the gauge indication even if present at relatively low level. In spite of these considerations, the quoted upper limit represents a factor three to five decrease of the H₂ outgassing measured for bare, vacuum fired stainless steel chambers.

Conclusion

Evidence has been obtained that low activation temperature coatings exist. The lowest measured activation temperature, for equiatomic thin film coatings of Ti and Zr, 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 any relevant performance deterioration. Large pumping speeds have been measured together with surface saturation concentrations of up to the 10¹⁵ molecules cm⁻² range. Precise pumping speed and saturation surface coverage measurements will be carried out in the near future.

The available results also provide information on the getter film effectiveness for trapping H₂ originating from the underlying substrate. This effect is present even in the absence of getter film activation, showing the interest of this solution even in the case of applications for which a baking temperature of 150°C cannot be exceeded.

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