

# Vacuum properties of palladium thin film coatings

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## Abstract

A recent development, carried out at CERN for particle accelerator applications, showed that a vacuum chamber coated with a thin getter film and then exposed to ambient air may be transformed into a pump by “in situ” heating at temperatures as low as 180°C.

Heating activates the diffusion into the film of the oxygen present in the surface passivation layer. Repeated air exposure–activation cycles progressively enrich the film with oxygen, reducing its performance and shortening its operating life. To overcome this inconvenience, noble metal coatings were considered. At distinction with getters, noble metals may release all the pumped gases by heating, resulting in a practically unlimited life.

Thin film coatings of palladium were studied by surface analysis, electron stimulated desorption and pumping speed measurements. These coatings were found to pump H<sub>2</sub> and CO, even without activation by heating, but not N<sub>2</sub> or CO<sub>2</sub>. Thin Pd and Pd–Ag films were also used as overlayers for protecting a getter film from oxidation while not impairing its H<sub>2</sub> pumping.

The result of these studies are presented and discussed.

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## 1. Introduction

Thin film coatings of non-evaporable getter (NEG) materials, produced by sputtering, were developed at CERN and extensively studied during the past few years [1–13]. These coatings strongly inhibit the outgassing of the underlying surface and, after activation, transform the coated surface into a pump. Activation temperatures as low as 180°C were achieved for TiZrV films, so

rendering activation compatible with the baking temperature of copper and aluminium alloy vacuum chambers.

Depending on coating characteristics, pumping speeds up to 11 s<sup>-1</sup> cm<sup>-2</sup> for H<sub>2</sub> and 101 s<sup>-1</sup> cm<sup>-2</sup> for CO were measured at room temperature, together with CO surface capacities up to 10<sup>16</sup> molecules cm<sup>-2</sup> [12]. Ultimate pressure limitations were not detected down to 10<sup>-13</sup> Torr, except those resulting from the presence of gases not pumped by NEG (i.e. methane and rare gases) and/or due to the measuring gauge outgassing [6].

This technology was developed for the demanding vacuum needs of particle accelerators, for which it provides a high, evenly distributed

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pumping speed, with the additional unexpected bonus of very low secondary electron yields [13]. However, NEG coatings could be conveniently used for other UHV applications, as for instance to improve the performance of turbomolecular and sputter-ion pumps, or for standard UHV components. Furthermore, they could also be adopted for electronic devices and more generally for any vacuum sealed device such as cryogenic dewars/transfer lines or evacuated solar collectors.

All the materials tested are based on the elements of the IV-B column of the periodic table, i.e. Ti, Zr and Hf. These elements provide oxygen solubility limits higher than 20% (atomic), i.e. higher by more than an order of magnitude than those of any other element at room temperature. Due to high binding energy, oxygen is not released by getters while heating. Therefore, repeated activation/atmospheric exposure cycles result in a progressive oxygen enrichment of the coating, which in turn limits its operating life. When assuming that the surface passivation layer consequent to atmospheric exposure contains the equivalent of 10 monolayers of oxygen, which is dissolved inside the coating during activation, an oxygen content at the percent level is established after five activation cycles of a film 1  $\mu\text{m}$  thick. Although also grain boundaries may participate to the oxygen uptake, the importance of a high solubility limit for oxygen is evident.

Due to the practical importance of these considerations, the performance variation (ageing) of NEG films, resulting from repeated activation/air venting cycles was extensively investigated. It was shown that a 5  $\mu\text{m}$  thick TiZrV film may undergo more than 50 such cycles with minor consequences [10], provided that the activation temperature is progressively increased from 200°C to 350°C.

Although reassuring, this result does not remove the problem. To do so, materials with little or no reactivity for O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O would be required. In this case not only the coating life would be unlimited, but also heating would not be mandatory for activation. The obvious price to be paid, however, would be a highly selective pumping.

Materials with these properties actually exist inside the family of noble metals. In particular,

palladium presents a negligible enthalpy of reaction with CO<sub>2</sub> and N<sub>2</sub>, while its low value for CO and H<sub>2</sub> allows these gases to be desorbed by heating. Palladium is particularly interesting also for its extremely high diffusivity and absorption capacity for H<sub>2</sub>, and therefore it has been privileged in our study. Platinum has also been submitted to exploratory tests, and the available results will be reported for comparison.

## 2. Experimental techniques

Coating was carried out by magnetron sputtering making use of a central cathode consisting of single wires 1 mm in diameter. Typical coating parameters were cathode voltage 500 V, discharge gas (argon) pressure  $2 \times 10^{-2}$  Torr, applied magnetic field 200 G, substrate temperature 100°C, coating rate 0.1  $\text{\AA s}^{-1}$  and film thickness about 0.5  $\mu\text{m}$ . A more detailed description of the coating process may be found in Ref. [1].

Samples of different size and geometry (small samples for surface analysis and cylindrical tubes for vacuum performance evaluation) were analyzed by Auger spectroscopy, electron microscopy, pumping speed measurements and electron stimulated desorption (ESD) of neutrals. As for the production procedure, the evaluation techniques were the same already used for NEG coatings and described in more details in Ref. [1].

## 3. Results

### 3.1. Surface analysis

As expected for noble metals, the Auger spectra of the air-exposed Pd films are widely different from those of most metals. The O-KLL line at around 515 eV, produced by the surface oxide, is in this case absent, even for as-received, not heated samples, showing that a stable surface passivation layer is not formed on Pd upon atmospheric exposure. However, a carbon surface contamination may be detected, very similar to that usually noticed for metal surfaces of different nature.

## 3.2. ESD

Important differences are also visible in the ESD results, shown in Fig. 1. In this figure the total pressure increase and the effective desorption yield variations as a function of the heating cycles for Pd, TiZr and stainless steel are compared. In all cases, the temperature dependence is much less pronounced for Pd than for the TiZr film, without any indication of activation onset. The absolute values for H<sub>2</sub> are extremely low, while for CH<sub>4</sub> they are similar to those of activated TiZr. The CO<sub>2</sub> yields are much higher, also due to the lack of pumping for this gas, while the yields of CO are not measurable because in the shadow of the CO<sub>2</sub> cracking pattern. Very

similar results (within a factor of 2) were obtained for Pt.

The origin of the dominant desorption yield for CO<sub>2</sub> deserves a complementary comment. Since this gas is not chemisorbed by Pd, its release cannot be imputed to a direct desorption mechanism, but rather to an electron-induced cracking of the carbonaceous surface contaminants.

If the sample is not heated (see Fig. 2) the desorption yields are initially about one order of magnitude higher than those measured after 120°C heating, and they decrease with increasing pumping time, reaching values 2–5 times higher after 50 h of pumping. Also in this case very similar results were obtained from Pt coatings.

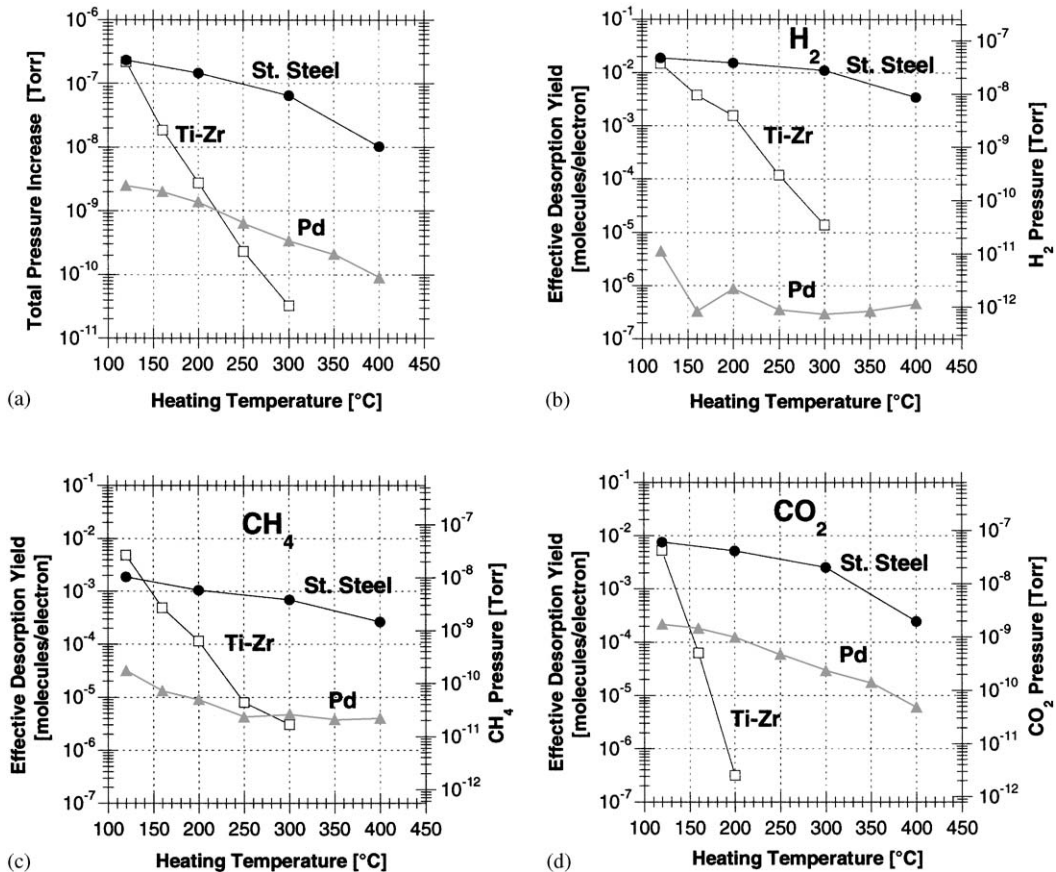


Fig. 1. Dependence of Pd coating ESD results on heating temperature (heating duration 2 h), compared to that from stainless steel and TiZr coating. The samples are bare and coated stainless steel cylinders 50 cm long and 10 cm in diameter. The energy of the bombarding electrons is 500 eV, the electron current 1 mA. The reported data are apparatus-dependent whenever sample surface pumping takes place because the competing action of desorption and sample pumping are not disentangled.

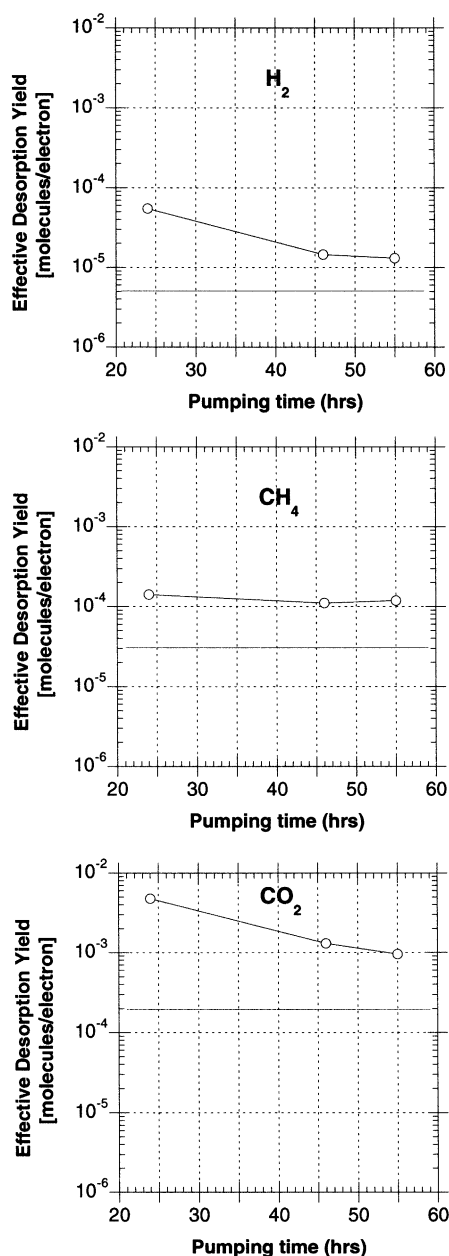


Fig. 2. Results obtained as described for Fig. 1 after different pumping times without sample heating. The horizontal lines correspond to the values measured after heating at 120°C.

### 3.3. Ultimate pressure and pumping speeds

The ultimate pressure was measured at the extremity of a 2 m long Pd-coated chamber of

160 mm diameter, connected at the other extremity to an UHV vacuum system via an orifice of 25 l s<sup>-1</sup> of conductance for H<sub>2</sub>. A detailed description of this system is given in Ref. [6].

The pressure measured after 24 h baking at 250°C was  $2 \times 10^{-13}$  Torr. The corresponding sticking factor for H<sub>2</sub> was higher than 0.15. This value was obtained by Monte Carlo simulation from the pressure attenuation across the chamber measured when the sample gas is injected at one of its extremities. Since only total pressure is measured, the presence of impurities cannot be excluded. If the impurities are not pumped by the Pd film, they adversely affect the pressure gradient and decrease the calculated sticking probability. This effect is more important for long, narrow chambers and injected gases pumped with high speed. Since both these conditions are present in our case, only a lower limit of the sticking probability could be given. For comparison, H<sub>2</sub> sticking probabilities of 0.5 are reported [15]. For the same reason, the sticking probability for CO could not be obtained; according to literature, it is very close to 1 [14].

Pumping speeds for H<sub>2</sub> were also measured for the unbaked Pd-coated chamber after different pumping times. Fig. 3 shows the H<sub>2</sub> pumping speed versus water vapour pressure, which steadily decreases while pumping. This result indicates that heating of Pd thin films is not required for H<sub>2</sub> pumping.

## 4. Pd coatings on NEG films

Although large H<sub>2</sub> quantities may be accommodated in Pd at high pressures, due to its low binding energies both for surface adsorption (about 1 eV) [15] and for solid solution (about 0.1 eV) [16], even small H<sub>2</sub> quantities result in dissociation pressures unacceptably high if compared to UHV standards.

A better situation might be achieved if the Pd film is coated over a predeposited NEG film as already reported for Pd coatings on bulk Nb and Ta [17]. In this case H<sub>2</sub> could migrate through the Pd to the NEG film, where it may be stored with a negligibly low dissociation pressure. For this

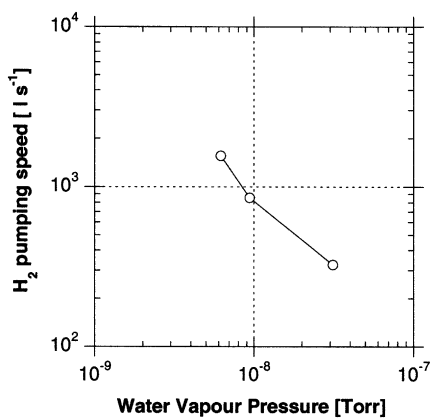


Fig. 3. Hydrogen pumping speed dependence on the water vapour pressure for the Pd coated sample of Fig. 1. The measurements were carried out using a Fisher–Mommson pumping speed dome after different pumping times in an unbaked vacuum system. Care has been taken to minimize the injected amount of  $H_2$  for pumping speed evaluation, so as not to affect appreciably the  $H_2$  surface coverage which in turn would result in a pumping speed reduction for the following measurements.

application, Pd might be advantageously replaced by PdAg alloys, which provide an easier transmission of  $H_2$  to the underlying NEG [18].

In order to explore this possibility, stainless steel vacuum chambers coated with Pd, Pd/NEG, and Pd70-Ag30/NEG, were exposed to various  $H_2$  loads (after bakeout at  $120^\circ\text{C}$  for 24 h) and then heated under static vacuum with a ramping rate of  $60^\circ\text{C/h}$ . The results are shown in Fig. 4.

The Pd film coated on stainless steel, even without any  $H_2$  injection, displays a steady pressure increase for increasing temperature. At distinction with this behaviour, in the case of Pd coated on a TiZr film, heating produces initially an increase of the  $H_2$  pressure, which then decreases down to the ultimate pressure of the system. This trend is common to the  $H_2$  loaded and unloaded Pd/NEG coated chambers, although with a slightly different  $H_2$  pressure peak temperature, showing that  $H_2$  may be fully transferred at temperatures lower than  $100^\circ\text{C}$ .

On the other hand, no pressure increase is detected for PdAg/NEG, in spite of the much larger injected  $H_2$  quantity, showing that no heating is needed in this case for transferring

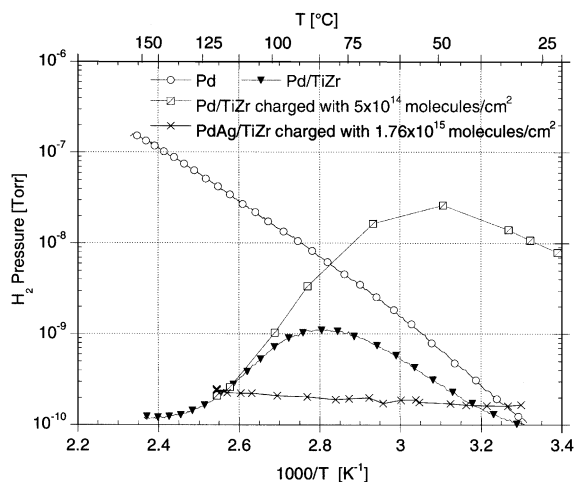


Fig. 4. Temperature dependence of the  $H_2$  pressure measured for different samples (same geometry as those of Fig. 1) submitted to different  $H_2$  loads and heated under static vacuum at a rate of  $60^\circ\text{C/h}$ .

$H_2$  to the NEG film due to the low activation barrier for  $H_2$  migration from the surface into the PdAg bulk and from the latter into the TiZr film.

## 5. Conclusions

On palladium thin film coatings exposed to ambient atmosphere a stable passivation layer is not formed.

The low binding energies for  $H_2$  and CO make their pumping thermally reversible, so allowing a practically unlimited operating life to be achieved. A similar behaviour is also displayed by Pt films, which however have not been studied at the same extent.

In order to compensate for the low  $H_2$  pumping capacity in the UHV pressure range Pd and PdAg coatings have been used as overlayers on NEG films. In this case both the higher sticking factor for  $H_2$  of Pd and the large  $H_2$  absorption capacity of NEGs are jointly available in a hybrid coating, which is ageing free and does not require heating for activation.

Such features make Pd/NEG and PdAg/NEG particularly suited for clean UHV systems which

are often vented to air and/or for pumping large quantities of H<sub>2</sub> in unbaked vacuum systems, where water vapour would otherwise completely saturate the NEG film. In this case, however, the coating should be kept warm enough during operation to prevent water vapour physisorption (about 100°C).

For particle accelerator applications, the hybrid coatings provide lower electron-induced desorption yields than the usual construction materials, and even than NEG coatings in the case of H<sub>2</sub>. On the other hand, no pumping is provided for CO<sub>2</sub>, and the secondary electron yields are intrinsically high (peak value of 1.4 even after heating at 350°C [19]). Before an application to a real machine could be envisaged, more work would be needed, particularly to explore the dynamic vacuum behaviour under electron/synchrotron radiation surface bombardment and the possible benefits of specific treatments to decrease CO<sub>2</sub> desorption.

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