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Getter pumping

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Abstract
A surface may provide a useful pumping action when able to retain adsorbed gas molecules for the duration of a given experiment. To fulfil this condition at room temperature, strong binding forces, as those resulting from chemical reactions, are required. Materials able to react with gases to form stable chemical compounds are called getters. The two main families of getters (evaporable and non-evaporable, or NEG) are presented and discussed. Special emphasis is placed on the NEG strips currently used for the vacuum systems of particle accelerators, and on the newly developed NEG thin-film coatings, in view of their possible future applications.

1 Generalities

1.1 Molecular mean free path λ

$$\lambda = \frac{7.3T}{10^{20}\pi r_0^2 p}\,\text{cm}$$

where T is the absolute temperature (K), p the pressure (Torr) and πr_0^2 the collision cross-section (cm^2). For N_2, $\pi r_0^2 = 4.26 \times 10^{-15}$ cm^2. At 295 K, $\lambda = 5 \times 10^3 p$ (i.e. 5 cm at 10^{-3} Torr, or 5×10^6 cm at 10^{-9} Torr).

Only molecular flow ($\lambda >>$ wall distance) will be considered hereafter.

1.2 Conductance and surface pumping

The conductance C of an orifice (zero wall thickness approximation) may be expressed as

$$C = 3.64\,(T/M)^{1/2}\,\ell\,\text{s}^{-1}\,\text{cm}^{-2}$$

with T = absolute temperature (K), M = molecular weight.

If all molecules impinging on a surface are captured, C represents the specific pumping speed S of the surface. More generally

$$S = \alpha 3.64\,(T/M)^{1/2}\,\ell\,\text{s}^{-1}\,\text{cm}^{-2}$$

where α is the *sticking probability* $(0 \le \alpha \le 1)$.

For $\alpha = 1$, $S \cong 44\ \ell\ \text{s}^{-1}\ \text{cm}^{-2}$ for H_2 and $S \cong 12\ \ell\ \text{s}^{-1}\ \text{cm}^{-2}$ for N_2 at room temperature.

1.3 Surface adsorption capacity

The monolayer capacity of an atomically flat surface is of the order of 5×10^{14} molecules cm^{-2}. If this monolayer of gas is released in a spherical volume of $1\,\ell$ (surface area ~ 500 cm^2) the pressure

increase would be 7 × 10^{-3} Torr. Therefore *surface degassing* is the main obstacle to achieving UHV conditions. Conversely under UHV conditions, *surface pumping* may be adopted.

1.4 Surface saturation time (monolayer formation)

Combining surface pumping speed and capacity, the surface saturation time t_{sat} becomes

$$t_{\mathrm{sat}} \cong 10^{6}\, p \;\text{ seconds } (p = \text{pressure in Torr})$$

when assuming sticking probability = 1, atomically flat surface, ambient temperature, N_2 gas (M = 28). Therefore, $t_{\mathrm{sat}} \cong 1$ second at 10^{-6} Torr under these assumptions.

1.5 Sojourn time, desorption probability

For a molecule adsorbed with a binding energy E on a surface at a temperature T the *probability of escape* ν is

$$\nu = \nu_0 e^{\frac{-E}{RT}} \;\text{(Frenkel, 1924)}$$

where ν_0 is an attempt frequency, of the order of the vibrational energy of the adsorbed molecules $\left(\nu_0 \cong 10^{13}\ \mathrm{s}^{-1}\right)$ and $R = 1.98\times10^{-3}$ kcal mole^{-1} K^{-1}.

It is often more useful to use the reciprocal of this term, $t = 1/\nu$, known as *mean sojourn time* or *mean surface lifetime*

$$\tau = \tau_0 e^{\frac{E}{RT}} \;.$$

Obviously, a surface provides a good pumping action when τ is much larger than the duration of the experiment. Typical values of τ are given in Table 1 [1]. Large τ values imply large E. However, surfaces providing low E values may display a useful pumping action when reducing the working temperature. The Frenkel equation is often used in its logarithmic form. By plotting the logarithm of the measured pressure versus 1/T, a straight line is obtained the slope of which defines the energy of the considered adsorption process.

Table 1: Mean stay time for adsorbed molecules at 300 K for various values of the adsorption energy, assuming $\tau_0 = 10^{-13}$ s

Energy (kcal/mol)	**Typical cases**	τ_a **(s)**
0.1	He	1.2 × 10^{-13}
1.5	H_2 physisorbed	1.3 × 10^{-12}
3.5–4	Ar, CO, N_2, CO_2, (physisorbed)	1 × 10^{-11}
10–15	Weak chemisorption	3 × 10^{-6}
	Organics physisorbed	2 × 10^{-2}
20	H_2 chemisorbed	100
25		6 × 10^{5} (1 week)
30	CO chemisorbed on Ni	4 × 10^{9} (> 100 yr)
40		1 × 10^{17} ($\approx$ age of the Earth)
150	O chemisorbed on W	10^{1100} ($\approx 10^{1090}$ centuries)

1.6 Gas-surface binding energies

Two types of forces may bind a gas molecule to a surface:

- *Chemical forces* involving electrons, e.g., hydrogen bonding, covalent or metallic bonding, characterized by binding energies typically in the range of some eV per molecule or larger than 10 kcal/mole (0.4 eV/molecule ≅ 10 kcal/mole).
- *van der Waals forces* of electrostatic nature, e.g., dispersion or polar forces, characterized by smaller binding energies, lower than 0.4 eV/molecule or 10 kcal/mole.

In the first case (*chemical adsorption or chemisorption*) long sojourn times are possible at room temperature (*getter pumping*). In the second case (*physical adsorption or physisorption*) pumping requires surface cooling (*cryopumping*) because the mean sojourn time at room temperature is too short (see Table 1).

1.7 Definition of getters and getter pump types

Getters are materials able to fix gas molecules on their surface in the form of stable chemical compounds. To do so, their *surface* must be *clean*. There are two ways of producing a clean gettering surface

- by *in situ* deposition of a fresh getter film,
- by heating an oxidized getter to a temperature high enough to diffuse oxygen from the surface into the getter bulk.

In the first case we speak about *evaporable getters*, in the second case about *non-evaporable getters (NEG)* and the required heating temperature is called *activation temperature.*

2 Evaporable getters

The two materials most widely used as evaporable getters are *barium* and *titanium* [2].

Barium is usually sublimated from a $BaAl_4$ alloy by heating at ~ 900°C. It is used for pumping vacuum sealed devices (electron tubes) and the sublimation is done in one single process before sealing. It is not used for UHV applications and will not be discussed here. For more details see Ref. [3].

Titanium is the most widely used evaporable getter for UHV applications. It is usually sublimated from filaments made of Ti alloys (with Mo or Ta) heated up to 1500°C, temperature at which the Ti vapour pressure is about 10^{-3} Torr. Titanium films provide *sticking probabilities* of $1–5 \times 10^{-2}$ for H_2 and 0.4–0.6 for CO at room temperature. Cooling to liquid N_2 temperature enhances these values to 0.1–0.3 for H_2 and about 1 for CO [4]. Other materials (Ta, Nb, V, Zr, Mo) have also been used, but their behaviour is not as good for various reasons [5].

Warning: Sticking probabilities reported in the literature for a given gas-getter combination present a large spread. Besides possible experimental errors, this spread has two distinct causes, namely:

- *surface roughness* which may result in a large number of molecule–surface interactions, i.e. higher capture probability.
- *initial surface contamination* which may reduce the adsorption site density available for pumping; this effect is particularly important for experimental systems which provide a base pressure higher than about 10^{-9} Torr and/or when the sticking probability is measured at high pressures (10^{-7}–10^{-6} Torr).

At room temperature all gases but H_2 adsorbed by a Ti film remain on the surface, resulting in a progressive reduction of pumping speed (surface blocking). On the contrary, H_2 diffuses and its pumping speed is not affected by the pumped amount. On the other hand, the high (> 30 kcal/mole) binding energies prevent the *desorption* of gases adsorbed on Ti at practically allowed temperatures. Again H_2 represents an exception, since its lower binding energy (~ 20 kcal/mole) allows desorption by heating (see Table 1).

The initial pumping speed of a Ti sublimation pump may be restored by a further sublimation process. The total *pumping capacity* is therefore very large and depends on the available amount of Ti in the filament. The *ultimate pressure* of a Ti sublimation pump is in principle not limited; in practice it may be spoiled by the presence of rare gases and methane if an adequate pumping for these gases is not foreseen.

In conclusion, Ti sublimation pumps provide the following advantages and disadvantages:

– *Advantages*: large pumping speed, large pumping capacity, unlimited ultimate pressure, compact, inexpensive, easily operated.

– *Disadvantages*: no pumping for inert gases, CH_4 production (?) and localized pumping (not very suitable for conductance-limited vacuum systems, as those of particle accelerators).

3 Non-evaporable getters (NEG)

NEGs are usually produced by fixing a powder of the getter material to a (metal) substrate by pressing, sintering or cathaphoresis [6]. After insertion in the system to be pumped, activation is carried out by heating. Usually NEGs are alloys of the elements of the IV B column of the Periodic Table, to which some of the actinides and rare earths may be added. Also Al is often added to increase the diffusivity of the adsorbed gases when heating. For more details on this subject see Ref. [7].

The performance of a given NEG is characterized by *activation temperature, sticking probability, surface capacity, total pumping capacity* (for H_2 and for heavier gases) and *particulate loss.* Since NEGs are highly porous (and the small grains are in poor contact with the substrate), the danger of *pyrophoricity* imposes a lower limit to the activation temperature (350–400°C). If compared to Ti sublimation pumping, NEG pumping presents the risk of *powder peel-off* (excessive heating or H_2 embrittlement) and a *lower pumping capacity*; however, NEGs may provide *linear pumping* and *passive activation*. If the activation temperature is compatible with the baking temperature of the chamber where the NEG is inserted, the getter may be activated during bakeout. This feature is particularly attractive because it removes the need of electric feedthroughs and powering/control systems and allows increasing the NEG surface and consequently its pumping speed. All NEGs available on the market are produced by *SAES Getters*. We will consider here only the types St 101 and the St 707 (Table 2), which are the best suited for UHV applications.

Table 2

	St 101 [8–10]	**St 707 [11, 12]**
Composition	Zr 84%, Al 16% (at. %)	Zr 70%, V 24.6%, Fe 5.4%
Getter layer thickness	~ 0.1 mm	~ 0.1 mm
Activation	750°C for about 30′	400°C for about 1 hour
Porosity	~ 10%	~ 10%
Substrate	steel or constantan	steel or constantan
H_2 dissociation pressure*)	$\log(p_{H_2}) = 4.28 + 2\log(q) - 7000/T$	$\log(p_{H_2}) = 5.14 + 2\log(q) - 6250/T$

*) Pressure p in mbar, H_2 quantity q in mbar ℓ g^{-1}, T in degrees Kelvin.

Note that the equilibrium pressure of H_2 over the St 707 (same temperature and H_2 concentration) is about two orders of magnitude higher compared to St 101.

Warning: Owing to its low activation temperature, the St 707 may be *ignited by spot welding*.

Both the St 101 and the St 707 have been extensively studied at CERN. The St 101 was selected to provide the main pumping for the Large Electron–Positron Collider (LEP) [13] (see Fig. 1).

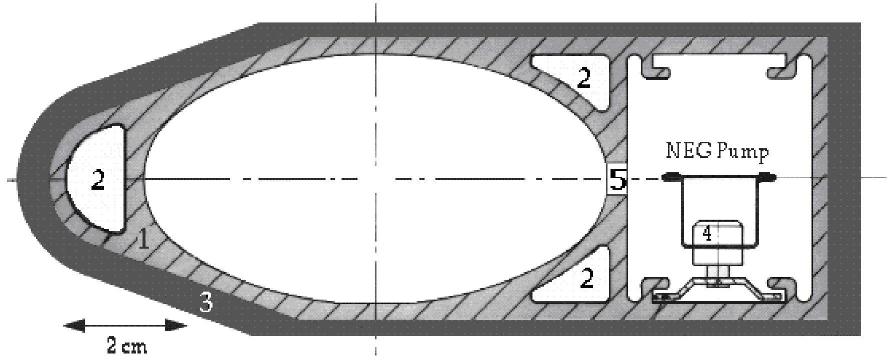

Fig. 1: Cross-section of the LEP dipole vacuum chamber

The main results are the following.

– Ultimate pressure

A LEP chamber 12 m long, made of Al alloy, baked at 150°C, pumped by St 101 and a sputter-ion pump of about 30 ℓ s^{-1} speed reaches an ultimate pressure of about 2×10^{-12} Torr, mainly due to Ar and CH_4, gases not pumped by the getter. By adding six additional sputter-ion pumps, a pressure of about 5×10^{-13} Torr (mainly H_2) is obtained [14] (see Figs. 2 and 3). Making use of the St 707 fully covering the inner walls of a 3 m long stainless-steel chamber of 160 mm diameter (see Fig. 4), pressures in the low 10^{-14} Torr have been achieved after passive activation during a 350°C bakeout [15].

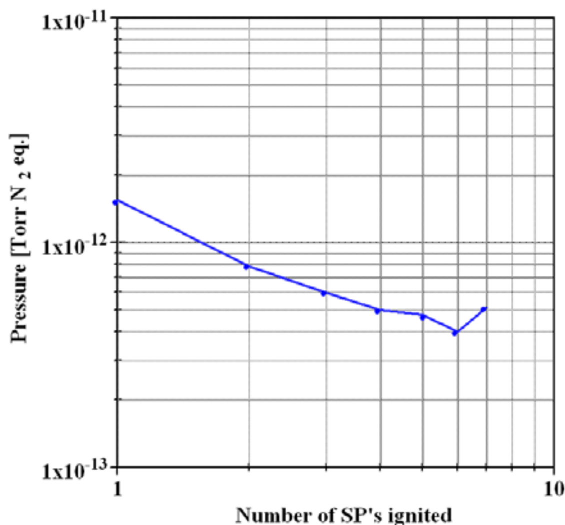

Fig. 2: Variation of the total pressure measured on a 12-m long LEP chamber equipped with a NEG pump and seven sputter-ion pumps, as a function of the number of sputter-ion pumps ignited

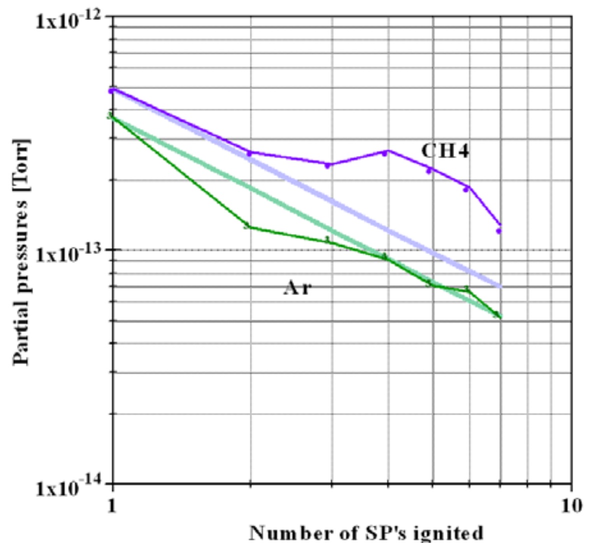

Fig. 3: Same variation as in Fig. 2, for the argon and methane partial pressures

Fig. 4: Schematic view of the St 707 'total' NEG pump

– Pumping speed variation as a function of the amount of pumped gas

The pumping curves obtained at room temperature for the St 101 [16], represented in Fig. 5, indicate that, after saturation of the external surfaces, the pumping speed is limited by the conductance to the internal pores of the getter coating. A mathematical model of the pumping process points out that, for a given gas load in the coverage range of practical interest, the NEG pumping speed is proportional to the square of the coating porosity. This model allows one to estimate the porosity from the *S*(*Q*) curves, in good agreement with the values obtained by direct porosity measurements. The developed model also predicts that CO is not dissociated on the St 101 (single-site adsorption) while H_2 is dissociated (two-site adsorption) as well as N_2, which, however, occupies six to eight adsorption sites. When *gas mixtures* are pumped [17], CO was found to inhibit the pumping of other gases, while N_2 has a small surface blocking effect and H_2 does not produce any blocking at all.

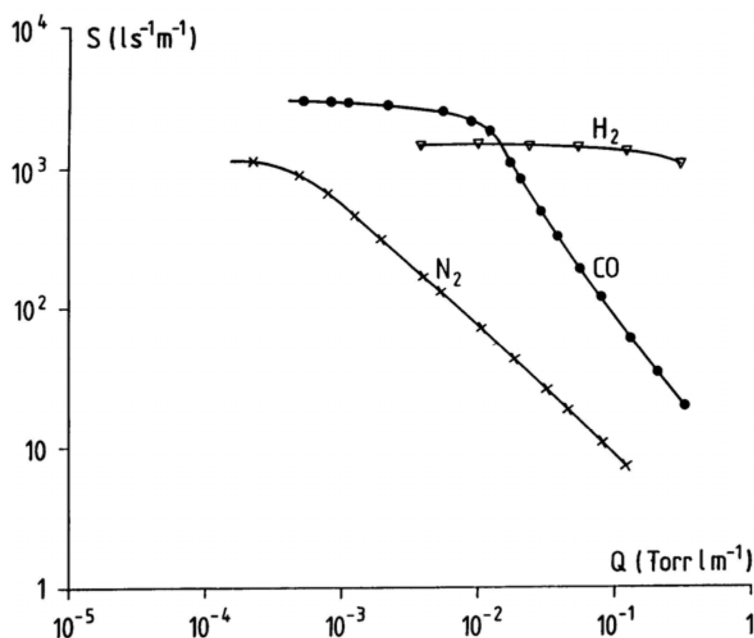

Fig. 5: Pumping speed variation of the St 101 NEG strip (30 mm wide) for H_2, CO, N_2 as a function of the amount of pumped gas

4 Thin-film getter coatings

Thin-film getter coatings, produced by sputtering, have been found to recover their chemical reactivity after exposure to ambient air followed by *in situ* baking [18, 19]. These coatings represent the last step of a process during which the pump has been moved progressively closer to the vacuum chamber walls. The getter thin-film coating actually transforms the vacuum chamber from a *gas source* into a *pump*.

Many metal coatings were studied at CERN, namely Ti, Zr, Hf, Nb, V and some of their binary and ternary alloys [18, 19]. The main goal was to reduce the activation temperature so as to allow activation also when using aluminium vacuum chambers, which cannot be baked at temperatures higher than about 200°C. This goal was achieved with a TiZrV alloy [20]. This alloy would be highly pyrophoric when used as a powder, but does not present this risk in the form of a thin film, thanks to the thermal stabilization provided by the much thicker substrate. The main results achieved using this coating are shown in Figs. 6 and 7. This study has been completed and the TiZrV coating has been applied to the vacuum chambers of many accelerators, and in particular to the warm sectors of the LHC at CERN.

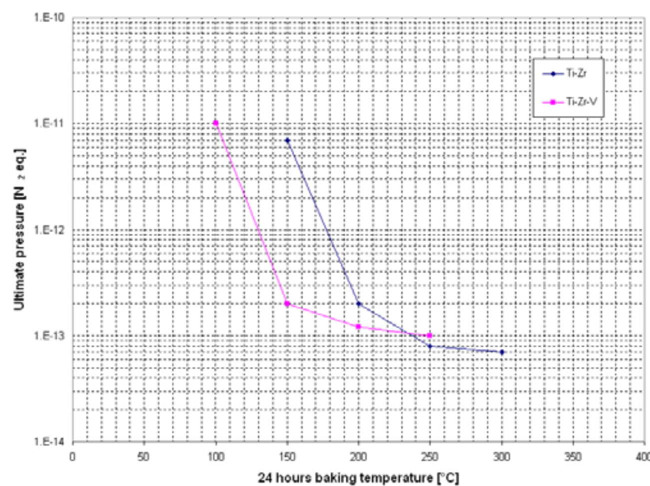

Fig. 6: Comparison of the ultimate pressures achieved in stainless-steel chambers coated with TiZr and TiZrV thin films. The chamber is 2 m long, its diameter is 100 mm, and it is connected at one extremity to a sputter-ion/titanium sublimation pumping station via an orifice of $25\,\ell\,s^{-1}$ conductance for H_2. The pressure is measured at room temperature at the opposite chamber extremity after a 24-hour baking at the indicated temperatures (without air exposure between bakeouts).

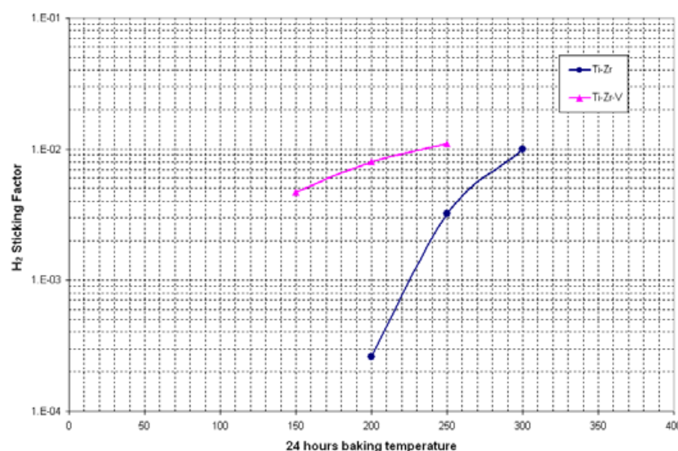

Fig. 7: Comparison of the H_2 sticking factors under the same conditions as described for Fig. 6

Compared to traditional NEG strips, the thin-film getter coatings provide the following advantages:

- reduced degassing
- lower activation temperature (200°C)
- wider choice of substrate possible
- materials may be produced which could not be produced otherwise (metastable and amorphous alloys)
- no space is required (coatings are a few microns thick)
- very low secondary electron emission.

In spite of being thinner than the powder coatings of traditional NEG strips by almost two orders of magnitude, thin-film getter coatings may provide pumping speeds and total surface capacities very similar to those of the St 707 NEG. They may also withstand many activation/air venting cycles without excessive performance deterioration. A TiZr film has undergone over 20 such cycles without losing more than 50% of its original pumping speed for H_2.

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