# NON-EVAPORABLE GETTERS: FROM PUMPING STRIPS TO THIN FILM COATINGS

C. Benvenuti, CERN, CH-1211 Geneva 23

*Abstract*

About 25 years ago, a study on the ultra-high vacuum behaviour of Non-Evaporable Getter (NEG) strips was undertaken at CERN. The resulting knowledge not only allowed NEG pumping to be successfully adopted for the LEP vacuum system, but was also essential for the development of niobium coated RF superconducting cavities later used to upgrade the LEP energy. Niobium is a powerful getter and its purity is mandatory to obtain superconducting cavities of the desired quality. Therefore stringent precautions must be adopted both for preparing the copper substrate and for the coating process itself. Very recently, the NEG pumping and the Nb coating techniques have been combined to produce thin film NEG coatings. Vacuum chambers sputter-coated with a thin film of a suitable getter material may be transformed from a gas source to a pump by activating the getter coating during standard "in situ" bakeout. As a result, the surface cleaned by this activation process presents a strongly reduced pressure rise under photon and/or particle bombardment. The material selection criteria, the coating procedure and the main results obtained to date are presented and discussed in view of the potential benefits of NEG coatings for accelerator vacuum systems.

## 1 LINEAR PUMPING BY NON-EVAPORABLE GETTER (NEG) STRIPS

In its standard configuration, a vacuum system consists of a chamber to which one or many pumps are connected by means of flanges. This configuration was adopted for all accelerators/storage rings built until the 70's. Even the very stringent vacuum requirements of the ISR at CERN could be fulfilled in this way, by applying "in situ" baking and short spacing between pumps.

The progressive reduction of the vacuum chamber aperture and the increase of the machine length, both due to increasing beam energy, rendered this "lumped" pumping approach very impractical, particularly in the presence of strong degassing induced by synchrotron radiation. Therefore, "integrated" linear sputter-ion pumps were developed, which were then used for PETRA at DESY[1], PEP at SLAC[2], TRISTAN at KEK[3] and HERA at DESY[4]. The "integrated" linear sputter-ion pumps make use of the machine dipole magnetic field, usually of the order of a few tenths of a Tesla. In the case of LEP however the field at injection energy is only $2 \times 10^{-2}$ T, a value dangerously close to the pump ignition threshold. Therefore, a linear NEG pump, not needing a magnetic field for operation, was preferred[5][6].

The adopted NEG pumping solution, covering about 23 of the 27 km of the LEP machine, relies on a 30 mm wide constantan strip coated on both sides with a 100 μm thick layer of Zr84-Aλ16 powder. The strip is commercially available from SAES-Getters under the trade name of St101[7][8]. A detailed description of the LEP pump may be found in Ref. 6. The linear NEG pump provides a pumping speed for $H_2$ of about 2000 $\lambda s^{-1}$ per linear meter, and produces an ultimate pressure of about $2 \times 10^{-12}$ Torr in a LEP dipole chamber after 24 h baking at 150°C. This limit is set by the outgassing of $CH_4$ and Ar, gases not pumped by NEGs, divided by the pumping speed of a sputter-ion pump (about 50 $\lambda s^{-1}$ nominal speed for a 12 m long chamber). When 6 such pumps are used on the same chamber, the measured limit pressure decreases to about $5 \times 10^{-13}$ Torr[9], as expected from the measured chamber $H_2$ outgassing and NEG pumping speed.

During machine operation however, large amounts of $H_2$, CO, $CO_2$ and $CH_4$ are extracted from vacuum chamber walls by synchrotron radiation, resulting in much higher pressures and in a progressive decrease of the pumping speed. At room temperature, the chemisorbed CO and $CO_2$ remain on the NEG surface where they inhibit further gas adsorption. Pumping speed may by restored by diffusing these gases into the getter by heating. Since NEG heating is not feasible during machine operation, intermittent heating must be applied. A large effort has been devoted to study the decrease of NEG pumping speed as a function of the quantity and nature of the pumped gases, in order to minimise the frequency of the heating cycles[10][11]. This study showed that porosity plays a dominant role in defining the room temperature NEG performance. Quantitatively, the pumping speeds for CO and $CO_2$ are proportional to the square of the NEG porosity for a given gas load and decrease proportionally to the gas load in the range of practical interest (from $10^{-2}$ to $10^{-1}$ Torr λ per meter of strip). Making use of a 6 parameter model developed for gas pumping simulation, it was possible to determine the porosity from the pumping speed curves, in excellent agreement with the value measured directly[10]. Thanks to the improved understanding resulting from this study and to a joint effort with the manufacturer, the porosity of the NEG coated strip has been increased from the initial 7% to 13% for the LEP delivery.

After exposure to ambient air, NEGs must be activated by heating. During activation the oxygen present in the

surface passivation layer diffuses into the bulk and a clean, active surface is obtained. Activation of the St 101 NEG requires heating to 750°C for about ½ hour; in the case of LEP, this is done by passing a current of 90 A through the strip. Obviously, resistive heating requires electrical feedthroughs and imposes electrical insulation. This limits the amount of strip which can be installed in a given volume, and therefore the available pumping speed.

Use of another NEG strip (St 707, also produced by SAES[12]), which only requires heating to about 400°C, makes activation feasible during (stainless steel) vacuum system bakeout. The pumping characteristics of the St 707 NEG have been studied in view of its use according to this "passive" activation process[13]. The results indicate that pumping curves very similar to those of the St 101 may be obtained after heating at 350°C-400°C. By completely covering the inner surface of a vacuum chamber with St 707 strip ("total" NEG pump), pumping speeds larger than $10^4\ \lambda s^{-1}$ per linear meter may be obtained after 350°C bakeout, resulting in pressures lower than $10^{-13}$ Torr[14]. Since the "total" NEG pump is modular, this result, obtained in a 3 m long stainless steel tube, may be extrapolated to vacuum systems of any length.

The evolution from the standard vacuum system configuration to the "total" NEG pump took about 20 years. Stimulated by the quest for larger pumping speeds and smaller pump dimensions, this evolution is characterised by a steady decrease of distance of the pump from the walls of the vacuum chamber. This approach results in more effective pumping, but does not reduce the gas load. A substantial decrease of degassing could be achieved if the pump is tightly joined to the walls, i.e. by coating the vacuum system with a NEG thin film to be passively activated during bakeout. This solution, if feasible, would represent the end point of the evolution described above.

## 2 NIOBIUM COATED RF SUPERCONDUCTING CAVITIES

At the end of the 70s, a vigorous R&D activity was started at CERN, aimed at developing superconducting accelerating cavities required to upgrade the LEP energy after completion of LEP phase I. At that time the accelerating field was severely limited by cavity "quenching" due to the poor thermal conductivity, at liquid He temperatures, of the niobium used as the construction material. To overcome this inconvenience, a study was launched in 1980 to replace the traditional "bulk Nb" with a "Nb on Cu" approach, consisting of a copper cavity internally coated with a thin film of Nb. It was hoped that this approach would provide a higher stability against quenching, thanks to the higher thermal conductivity of copper, and also allow a substantial cost reduction[15].

The development of the Nb coating, done by sputtering, has been carried out in parallel with that of the NEG pump for LEP. The first successful coating of a single cell, 500 MHz cavity was done in 1983[16]. The advantages hoped for were confirmed and some others unexpectedly discovered, such as higher quality factors $Q_o$ at 4.2 K (about a factor 2) and insensitivity to the earths magnetic field (thus eliminating the need for shielding or compensation coils)[17]. In 1990, orders were placed for industrial production of Nb coated copper cavities of 352 MHz frequency. The specified performance was $Q_o \geq 4 \times 10^9$ at 4.2 K and 6 MV/m, i.e. higher than for "bulk Nb" cavities ($Q_o \geq 3 \times 10^9$ at 5 MV/m). The 256 cavities of this type installed in LEP are now working smoothly and their accelerating field will be progressively increased toward 7 MV/m. We do not intend to expand here on these widely publicised results[17][18] nor on the behaviour of these cavities during operation in LEP[19]. Rather, we will discuss some important aspects of the production of the Nb coatings and emphasise their strong mutual influence with NEG pumping.

A literature search carried out in 1980 on Nb coatings produced by sputtering found only five papers. The reported critical temperature of the Nb films was generally 8.5 K (bulk value 9.3 K)[20][21][22] and their Residual Resistivity Ratios (RRR) values were rather poor (lower than 3), indicating a very short electron mean free path due to a high impurity content, which must be lower than 1% to obtain coatings of a reasonable RF quality. The purity of the film depends on the rate of arrival on the sample of both Nb atoms (usually of the order of 1 monolayer per second) and gas molecules (~1 monolayer per second at $10^{-6}$ Torr) which Nb, being a powerful getter, will trap. When a small sample is coated inside a large unbaked vessel an impurity level between 1% and 10% may be expected. These considerations led us to apply a bakeout prior to coating (ultimate pressure below $10^{-9}$ Torr) and to carefully minimise all possible gas sources. This implies in the first instance that the cavity is used as a discharge chamber. Although the cavity itself may act as a gas source initially, its outgassing is quickly eliminated as soon as a few monolayers of Nb have been deposited. Special care has also been devoted to the cavity surface cleaning and to the conditioning of the Nb cathode. Thanks to these precautions, $T_c$ values higher than 9.3 were regularly obtained together with RRR values up to 80. Even higher values were obtained in other laboratories[23] using this same strategy.

Although it was later discovered that such high RRR values are of no practical interest for superconducting cavities (they are even detrimental because the BCS surface resistance displays a broad minimum for RRR ≈ 10)[24] they could be extremely useful in other fields such as the production of Josephson junctions, where RRR values of about 4 are still currently obtained in spite of coating procedures optimised to produce the highest possible value[25].

Niobium coated copper is an interesting example of a "composite" solution in which copper is the structural

material and niobium the functional material. Composites are a growing issue in modern material science. Role splitting allows performances out of the reach of monolithic materials to be obtained. In the present case only the structural improvement has been exploited since the superconducting material is still niobium. However, the way is open for coatings possibly providing a superior superconducting behaviour to further improve cavity performance.

The development of Nb coated Cu cavities has produced, as a by-product, the competence required to design sputtering configurations adapted to any substrate geometry and the capability of producing high purity getter coatings. Furthermore, it represents a successful example of composite solution.

These are the basic ingredients which were needed before NEG coatings could be dreamed of.

## 3 THIN FILM NEG COATINGS

A thin film coating, to be passively activated during vacuum baking, would provide reduced degassing and surface pumping without requiring any additional space. Passive activation obviously implies a "bakeout compatible" activation temperature, i.e. a large oxygen diffusivity to dissolve the surface passivation layer at low temperature. Furthermore, the selected material should also provide a high solubility limit for this gas in order to accommodate its accumulation due to many activation/air venting cycles, a high reactivity for the main gases to be pumped ($H_2$, CO, $CO_2$) and high capacity and low dissociation pressure for $H_2$.

Many elements provide good gettering properties, but only those of the IV B column of the Periodic Table fulfil all these requirements, particularly the most restrictive one of the high solubility limit, which only for these elements exceeds 10%. Therefore, Ti, Zr, Hf and some of their binary combinations have been taken as an obvious starting point for an experimental study initiated at the end of 1995 [26][27].

Coatings have been produced by sputtering (magnetron configuration), which is simple and applicable to a wide range of materials, for which it preserves the stoichiometry. Sputtering has allowed alloys/compounds to be produced (and also metastable or amorphous alloys which could not be obtained otherwise) by using composite cathodes, prepared by intertwisting wires of elemental composition readily available on the market.

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 appropriate means to monitor the 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 all been used to characterize the coated samples and the information obtained from these three different methods was found to be mutually consistent[26][27]. An independent, complementary evaluation may be obtained by measuring the dependence of the ultimate pressure on baking temperature in a system where a large coated surface is pumped with a known and low pumping speed. By combining gas injection and Monte Carlo simulation, this system also allows molecular sticking coefficients to be determined[28].

Among the coatings of pure Ti, Zr, Hf and their equiatomic combinations, the lowest activation temperature was found for TiZr. A subsequent variation of Ti and Zr content did not result in any further reduction of activation temperature, therefore the equiatomic TiZr alloy has been fully characterized with the following results[26][27].

The ESD measurements obtained from coated stainless steel chambers after 2 h heating at different temperatures are shown in Fig. 1[26]. For elemental coatings no degassing variation is noticeable up to 200°C, while TiZr displays an activation onset at 150°C and is fully activated at 300°C.

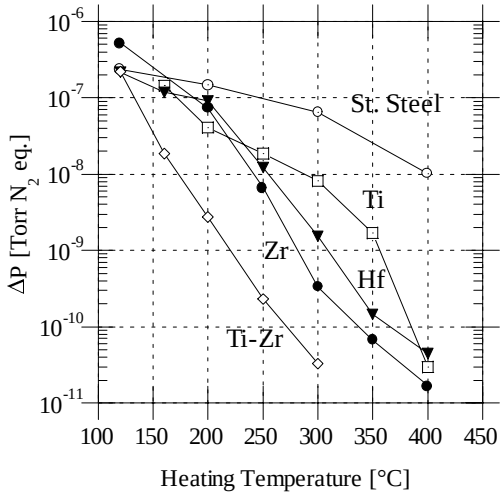


**Fig. 1:** Total pressure increase induced by electron bombardment of stainless steel, uncoated or coated with Ti, Zr, Hf, and equiatomic TiZr.
The measurements are carried out at 20°C after sample heating for 2 h at the indicated temperature without intermediate air venting. Electron energy 500 eV, electron current 1 mA.

The effective desorption yields of the various gases for a TiZr coated chamber are shown as a function of the heating temperature in Fig. 2. Note that for $H_2$, CO and $CO_2$ the measured values result from the competing effects of degassing and surface pumping, and consequently the observed decrease depends on the adopted experimental apparatus (for more details see ref. 26). Methane on the contrary is not pumped by getters, therefore its degassing decrease provides absolute

information on the progressive surface cleaning. Pumping speed measurements carried out on the same apparatus by gas injection indicate that $H_2$ pumping becomes appreciable after 250°C heating, while for CO pumping starts already after heating at 200°C. Extending the heating time from 2 h to 24 h roughly corresponds to increasing the 2 h heating temperature by 50°C[26]. Finally, ESD measurements indicate only marginal changes when applying up to 5 activation/air venting cycles[26].

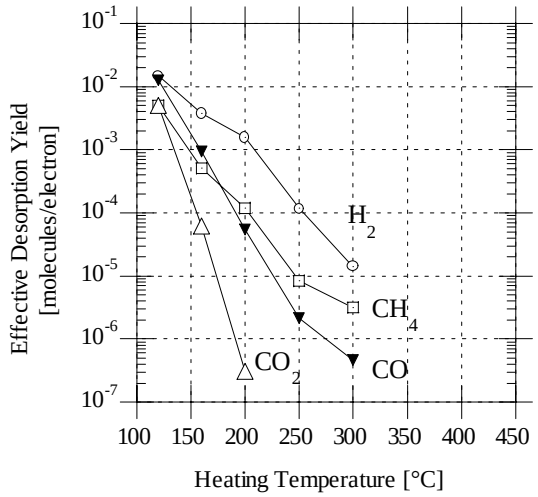


**Fig. 2:** Effective desorption yield of $H_2$, $CH_4$, CO, $CO_2$ for an equiatomic TiZr coating. Experimental conditions as described for Fig. 1.

Very recently (December 1997) a substantial decrease of activation temperature has been obtained by adding a vanadium wire to the Ti and Zr wires previously used for the cathode. The results obtained by ESD for TiZr and TiZrV are compared in Fig. 3[28], showing that the addition of vanadium shifts activation to a temperature about 50°C lower. This decrease is observable for all degassing products ($H_2$, CO, $CO_2$, $CH_4$)[28].

The decrease of activation temperature obtained by adding V is also visible in Fig. 4, where the ultimate pressures obtained after baking coated stainless steel tubes at various temperatures are compared, and in Fig. 5, where the comparison is extended to sticking coefficients for $H_2$ obtained by gas injection and Monte Carlo simulation.

The emerging global picture indicates that TiZrV is practically fully activated after 24 h baking at 200°C. This coating is quite robust with respect to repeated activation/air venting cycles (5 such cycles are possible at practically constant performance).

Last but not least, secondary electron yield measurements indicate that both fully activated TiZr and TiZrV present a peak value of about 1.1 and that subsequent saturation by exposure to CO, $CO_2$ and $H_2O$ does not increase this value by more than 10%[29].

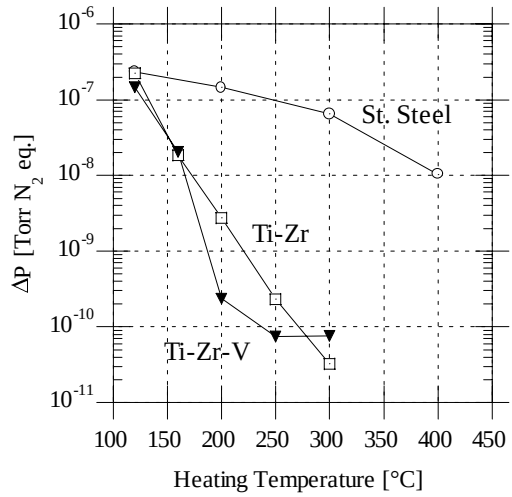


**Fig. 3:** Comparison of ESD measurements for stainless steel, TiZr and TiZrV coatings. Experimental conditions as described for Fig. 1.

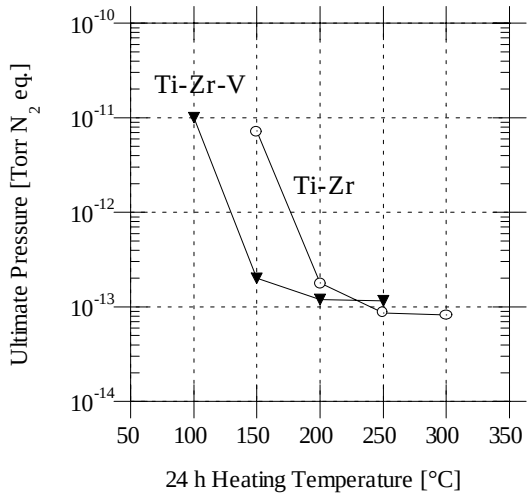


**Fig. 4:** Ultimate pressures obtained after 24 h baking cycles, without intermediate air venting, on chambers coated with TiZr and TiZrV. Chamber length 2 m, diameter 10 cm, applied pumping speed 25 $\lambda s^{-1}$ for $H_2$.

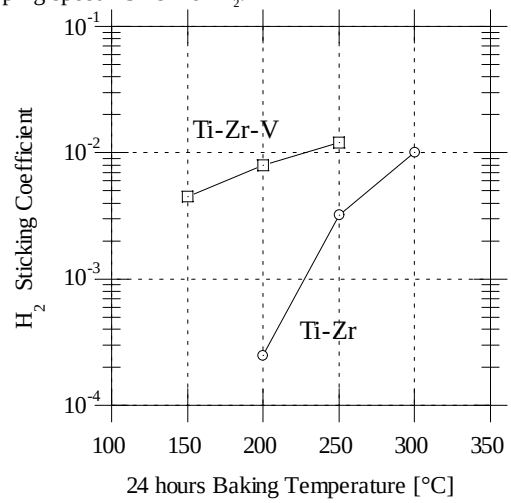


**Fig. 5:** Variation of the $H_2$ sticking coefficient for TiZr and TiZrV coated chambers as a function of baking (24 h) temperature. Data obtained by gas injection and Monte Carlo simulation.

## 4 CONCLUSIONS

The transformation of the vacuum chamber to a pump by NEG coating marks the end point of the accelerator vacuum system evolution described in this report.

Getter coatings reduce both static and radiation induced degassing, provide pumping without requiring additional space or equipment, do not impair vacuum chamber transparency for particles or surface impedance and inhibit electron multipactoring. They are ideally suited for Storage Ring applications, both for the experimental regions where pumps of other types cannot be installed to provide the required vacuum stability, and for the arcs where they would shorten the initial period required for vacuum conditioning from months to days. In a fully coated machine, radiation will only displace gas molecules already present on the NEG surface, of which the gas coverage should remain constant, a feature which should remove the need for intermittent NEG heating.

Getter coatings suffer from ageing due to activation/ venting cycles, an inconvenience which may be partially cured by venting accelerators with pure inert gases, but which may exclude application to laboratory vacuum systems routinely opened to air.

Niobium coated accelerating cavities and NEG coated vacuum chambers are typical examples of a composite solution obtained by combining a structural material with a functional material. Composites, a fast growing field in modern material science, are a powerful way to obtain properties out of the reach of monolithic materials but require a multidisciplinary approach and a long development time which usually is not available when the need first materializes. Therefore rationalisation of the efforts and anticipation of the needs will be essential to provide other innovative solutions to Particle Accelerator problems, which might also later produce important industrial spin-offs.

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