Evaluation of Ti-Zr-V (NEG) Thin Films for their pumping speed and pumping Capacity

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Abstract. Deposition of NEG thin films onto the interior walls of the vacuum chambers is an advanced technique to convert a vacuum chamber from a gas source to an effective pump. These films offer considerably large pumping speed for reactive gases like CO, H₂ etc. A UHV compatible pumping speed measurement system was developed in-house to measure the pumping speed of NEG coated chambers. To inject the fixed quantity of CO and H₂ gas in pumping speed measurement set-up a calibrated leak was also developed. Stainless steel chambers were sputter coated with thin film of Ti-Zr-V getter material using varied parameters for different compositions and thickness. Pumping capacity which is a function of sorbed gas quantities was also studied at various activation temperatures. In order to optimize the activation temperature for maximum pumping speed for CO and H₂, pumping speeds were measured at room temperature after activation at different temperatures. The experimental system detail, pumping performance of the NEG film at various activation temperatures and RGA analysis are presented.

1. Introduction
Non evaporable getters (NEG) are widely used to effectively capture molecules impinging on their active surface. Due to small vacuum chamber conductance and the particle induced desorption of gas molecules from chamber surfaces in the particle accelerators or storage rings, the required vacuum levels are difficult to maintain. An effective solution to overcome these problems is to coat the whole inner wall of the vacuum chambers with NEG film. On exposure to air, the NEG surface is covered by gases and become inactive. However, the surface may be activated by heating it. Thus the walls of the vacuum systems may be converted to a pumping surface and after insitu activation by baking these films provide a large pumping speed. The Ti-Zr-V coating has the attractive feature of a low activation temperature [1]. The NEG thin film was deposited using Ti-Zr-V getter material in a DC magnetron sputtering system developed in house[2]. From vacuum system designer’s point of views, the pumping speed and pumping capacity are very important vacuum parameters and these studies were conducted for H₂ as well as CO. Two SS chambers, coated with different coating parameters, were studied.

2. Description of the pumping speed measurement system
The experimental set-up developed and used for pumping speed and pumping capacity measurement of NEG coated chambers is shown in figure 1. The NEG coated SS chamber was installed on the speed measurement setup. One end of the coated chamber was connected to the gas inlet chamber and other end was connected to another SS chamber and a sputter ion pump (SIP) of 70 l/s pumping speed, through the orifice. The orifice conductance was 3.27 l/s for CO gas and 12.2 l/s for H₂ gas. On both side of the orifice, the chambers had Bayard Alpert Gauges and residual gas analysers (RGA) for total and partial pressure measurements. To check the pumping performance, CO and H₂ gases were injected through a calibrated leak valve. In order to reduce any outgassing from the other components
in the testing apparatus, pumping was provided by the turbo molecular pump (TMP) during baking. After baking, system was pumped by the SIP during activation and to achieve ultimate vacuum.

The pumping performance of the Ti-Zr-V coated stainless steel cylindrical chamber was evaluated by pumping speed and pumping capacity [3]. The pumping speed measurement of the NEG coated chamber was studied for CO and H₂ gas. These gases were individually introduced from the calibrated leak valve. The pressure in the gas reservoir was kept constant at almost 200 mbar. The pressure of the NEG chamber P₁ and that on other side of orifice P₂ were recorded during injection of the gas. The pumping speed of the NEG coated chamber was calculated from the measured P₁ and P₂:

\[ S_{NEG} = \frac{Q_L - C (P_1 - P_2)}{A} \]  (l/s-cm²)

Where,  
- P₁, P₂ are pressure on both side of orifice in mbar  
- C = Conductance of orifice  
- A = Coated surface area of the SS chamber (cm²)  
- Qₐ is the calibrated leak of the test gas which was kept at 2x10⁻⁶ mbar.l/s for CO and 2x10⁻⁵ mbar.l/s for H₂.

The total quantity of gas pumped Q̄sorbed was calculated from the equation

\[ Q_{sorbed} = \int (S_{NEG}. P_1) \, dt \]

Pumping capacity was evaluated by finding out the quantity of gas which was adsorbed at particular value of pumping speed.

3. Calibrated leak and gas inlet setup

The pumping speed measurement was done by injecting the gas through a calibrated leak valve at known leak rate which was developed for the test gases CO and H₂. The gas inlet system with calibrated leak is shown in figure 2. There is a gas reservoir container of nearly 2 litres volume, it had four ports to install Bourdon Gauge, leak valve, and two high vacuum right angle valves to connect TMP and gas cylinder. This bakable gas inlet setup was used to flush the system with test gas and also to inject the known quantity of gas into the pumping speed measurement system.

Leak valve calibration - The test gas was filled in a reservoir at 200 mbar pressure which was measured by a Burdon Gauge. At a particular opening of the leak valve, gas was leaked from the reservoir to speed measurement setup which had an orifice of conductance C. Pressure P₁, P₂ on both
side of the orifice were noted down at the time of injection of gas at particular opening of leak valve. During this measurement pumping was provided by the TMP. For a particular opening of the leak valve, specific leak \( Q_L \) was obtained which is given by \( Q_L = C (p_1-p_2) \). For different opening of leak valve different specific leaks were measured as given in table 1. UHV leak valve was calibrated for CO and H\(_2\) gas by filling the reservoir with CO and H\(_2\) respectively. This experiment was also performed using the helium (He) gas. The reservoir was filled with the He gas at 200 mbar and He gas was injected through leak valve into a chamber whose other port was connected to leak detector calibrated with standard leak for He. The He leak rate measured by LD was used to match leak rate for CO with correction factor.

| Leak valve opening | Specific leak (mbar-l/s) |
|--------------------|------------------------|
|                    | CO         | H\(_2\)   |
| Mark-I             | 4x10\(^{-7}\) | 6x10\(^{-6}\) |
| Mark-II            | 2x10\(^{-6}\) | 2x10\(^{-5}\) |
| Mark-III           | 7x10\(^{-6}\) | 8x10\(^{-5}\) |

4. Experimental procedure for pumping speed measurement

The two SS chambers of 100 mm diameter and 400 mm length were coated in the DC magnetron coating system [4]. These were chemically cleaned, electrolyplished and vacuum degassed. The chamber \#D (CH \#D) was coated with target made of Ti-Zr-V wires in ratio of 1:2:2 and the coating parameters were -600V discharge voltage, 200 gauss solenoid field, 2x10\(^{-2}\) mbar argon gas pressure, 150mA discharge current and 150°C substrate temperature. For CH \#D, the film deposition rate was 0.2 \( \mu \)m /hr, film thickness formed was nearly 1.65 \( \mu \)m and the composition of the NEG film in atomic percentage was Ti-25\%, Zr-27\%, and V-48\%. The chamber \#E (CH \#E) was coated with target made of Ti-Zr-V wires in ratio of 1:1:1 and the coating parameters were -600V discharge voltage, 200 gauss solenoid field, 1.2x10\(^{-2}\) mbar argon gas pressure, 100mA discharge current and 150°C substrate temperature. For CH \#E, the film deposition rate was 0.15 \( \mu \)m /hr, film thickness formed was nearly 1.62 \( \mu \)m and the atomic composition was Ti- 35\%, Zr-22\%, V- 43\%. The effective NEG coated area of both SS chambers was almost 1000cm\(^2\).

The NEG coated chamber was installed on the pumping speed measurement setup and leak tested. Initially the system was pumped by the TMP for 12 hrs and then whole system except the NEG coated chamber was baked at 250°C for 24 hrs. The temperature of coated chamber was maintained at 100°C to avoid NEG activation. This also avoided saturation of NEG from the gases released during bakeout. At the end of baking, as the temperature of system was reduced to 100°C the temperature of NEG coated chamber was increased to 150°C for 24 hrs while the temperature of the rest system was gradually decreased. Figure 3 shows the temperature profile. Gauges and RGAs were degassed at the end of the baking process, after baking system was pumped by the SIP. After cooling down to room temperature, the test gas was injected into the system for pumping speed measurement.

In a standard measurement cycle, the coated chamber was heated for 24 hrs at every activation temperature and the pumping speed for individual gases were measured after cooling down of system to room temperature. The pumping speed was measured at different activation temperatures in steps of 50°C from 150°C to 350°C for 24 hrs without air venting in between. During speed measurement, system pumping was provided by the SIP. After each activation when the coated chamber cooled down to ambient temperature, the test gas was introduced into the system and the pressures \( P_1, P_2 \) were recorded until the saturation of NEG film. To avoid accumulation of CH\(_4\) and rare gases, the system was continuously pumped with SIP.

5. Results

5.1. Ultimate Vacuum & RGA of NEG chambers

During the CO pumping speed measurement of NEG coated chamber, the coated chamber was heated at different activation temperatures. After each activation and before injection of CO, the NEG coated chamber was tested for ultimate vacuum. As the activation temperature was increased to 200°C, there was a sharp improvement in the ultimate vacuum in the NEG coated chamber. The ultimate vacuum
was achieved for CH #D and CH #E at different activation temperature is shown in figure 4. In the ultimate vacuum testing setup [5], the ultimate vacuum 7x10^{-12} mbar was achieved in CH #D, after activation at 300°C for 2hrs.

After activation at 150°C and 250°C temperature, NEG chamber was cooled down to room temperature and then the residual gas analysis was also performed. The residual gases present in the NEG coated CH #D and for CH #E are shown in figure 5 and figure 6 respectively. After 150°C activation the CO partial pressure (PP) was large compared to methane peaks, which was nearly the same as that for uncoated well baked vacuum chamber. This showed that the NEG surface was not activated at 150°C. As the coated chamber was activated at 250°C and cool down to room temperature, the partial pressure of CO was reduced compared to PP of CH₄ and its value reduced to 3x10^{-12} mbar for CH #D and 1.2x10^{-12} mbar for CH #E. This shows the activation of the NEG chamber for CO and it also indicated that the NEG film has negligible pumping speed for CH₄. Except H₂ all peaks were nearly to 1x10^{-12} mbar for CH #E, in RGA spectra.

5.2. Gas release during activation process
After CO pumping speed at particular activation, the system was pumped by the SIP for almost 24 hrs and then coated chamber was again heated to activate at next higher activation temperature. During the activation, the changes in the partial pressure of CO and H₂ are shown in figure 7. The initial PP of H₂ was 1.5x10^{-9} mbar and for CO it was 2x10^{-11} mbar. As the temperature was raised H₂ partial pressure continuously increased. But there was a small increase of CO partial pressure and as the temperature reached to 200°C the surface started pumping and PP of CO reduced further. At 250°C PP of CO increased slightly in 10^{-11} range, then as the chamber cooled down to room temperature it reduced to 10^{-12} mbar range. However during activation mainly H₂ gas was desorbed.
5.3 Pumping performance of CH #D.

At first the CO pumping speed of NEG chamber was measured at various activation temperatures and it was plotted as a function of the adsorbed gas load $Q_{\text{sorbed}}$ is shown in figure 8. After activation at 250°C, a pumping speed of nearly 0.7 l/s/cm$^2$ for CO was achieved; this was comparatively higher than that at 200°C activation. It was also observed that as the activation temperature was increased the pumping capacity also increased as shown by the $Q_{\text{sorbed}}$ quantity in figure 8. At 350°C pumping capacity slightly reduced because large quantity of CO gas was already pumped by the NEG film. The pumping speed remained nearly constant upto nearly $1\times10^{-5}$ mbar.l/cm$^2$ of sorbed gas quantity. After that it reduced very fast.

After completing the pumping speed measurement for CO, the whole setup was baked for 48 hrs and then same procedure followed for pumping speed measurement using H$_2$ gas. Figure 9 shows the H$_2$ pumping speed after activation at different temperatures. Compared to CO, H$_2$ pumping speed was less. But the pumping capacity for H$_2$ was high; H$_2$ pumping speed was nearly constant upto nearly $5\times10^{-3}$ mbarl/cm$^2$ of sorbed gas quantity after activation at 300°C. As shown in figure 8 and figure 9, pumping capacity for H$_2$ was larger than that for CO, due to different pumping mechanism for CO and H$_2$. CO molecules were only pumped by chemisorptions process onto the NEG surface and it was irreversible process. But the H$_2$ molecules were pumped by the diffusion process into the NEG film.

5.4 Pumping performance for CH #E.

For CH #E, the CO pumping speed of NEG chamber was measured at various activation temperatures. The CO pumping speed was plotted as a function of the $Q_{\text{sorbed}}$ as shown in figure 10. After 300°C activation, CO pumping speed of 1.85 l/s-cm$^2$ was achieved. There was not much difference in pumping speed at 250°C and 350°C activation temperature. It indicated that the NEG surface was fully activated at 250°C. At the same time as the activation temperature was increased the pumping capacity also increased as in figure 10. The pumping speed remained nearly constant upto $2.3\times10^{-5}$ mbarl/cm$^2$. After that it reduced very fast.
After CO pumping speed measurement for CH #E, H₂ pumping speed was measured at different activation temperatures is shown in figure 11. The H₂ pumping speed was 0.22 l/s-cm² after 250°C activation and after 400°C activation it increased to 0.65 l/s-cm².

The comparison of initial CO and H₂ pumping speed for CH #D and CH #E at various activation temperatures is shown in figure 12. The CO pumping speed increased as the activation temperature was increased. Initially, the H₂ pumping speed increased marginally but after activation at 400°C there was large increase in H₂ pumping speed. NEG coated chambers have low pumping speed for H₂ compared to CO. The CO pumping speed and capacity for CH #E were large compared to those for CH #D at same activation temperatures.

6. Conclusion
A UHV compatible speed measurement set-up was developed in house for studying important vacuum parameters like pumping speed and capacity for the NEG coated films. These measurements were successfully conducted for chambers coated with different coating parameters. The NEG coated chamber #E provided large pumping speed and capacity compared to CH #D. The observed activation temperature for the NEG coated chamber was 200°C to 250°C. It was found that the gases present in NEG pumping volume were mainly H₂ and large reduction of CO was observed. PP of CH₄ was high comparable to CO, as NEG had low pumping for it.

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