Characterization of titanium-zirconium-vanadium non evaporable getter coated vacuum chambers

K V A N P S Kumar¹, T Bansod¹, C Mukherjee², G Singh³, Pragya Tiwari⁴, B K Sindal¹ and S K Shukla¹

¹Ultra High Vacuum Technology Division, RRCAT, Indore - 452 013
²Mechanical & Optical Support Section, RRCAT, Indore-452 013
³Laser Material Design & Development Section, RRCAT, Indore- 452 013
⁴Indus Synchrotron Utilization Division, RRCAT, Indore- 452 013

E-mail: kkumar@rrcat.gov.in

Abstract. Non evaporable getter (NEG) coating technology development started at UHVTD, Raja Ramanna Centre for Advanced Technology (RRCAT). An UHV compatible, cylindrical magnetron sputtering system for Ti-Zr-V (Titanium-Zirconium-Vanadium) NEG coating was designed, developed and successfully installed at UHVTD, RRCAT. Surface studies play important role in this technology development. Inside surfaces of many vacuum chambers were coated with varying thickness and compositions using this setup. Preliminary studies of adhesion, crystallographic structure & size of crystallites, surface morphology, trapping of argon gas during coating and its release after getter activation were carried out and some results are reported in this paper.

1. Introduction

Getter coatings are chemical pumps which are able to chemisorb the active gases on their surfaces. The alloys of titanium, zirconium, vanadium and Iron are the most commonly used getter materials used in accelerators.

To coat the inner surfaces of vacuum chamber, magnetron sputtering is the most efficient method thus ensures better adhesion and microstructure formation. An UHV compatible, cylindrical magnetron sputtering system for NEG coating was designed and developed in house at UHVTD, RRCAT, India [1]. Using this system, many chambers were coated with varying thicknesses of NEG films [2]. The characteristics of NEG thin films in terms of microstructure, adhesion, surface roughness, grain formation was studied. The barrier effect of NEG coating in controlling hydrogen (H₂) outgassing from the system was also observed. The phase formation and crystallite size was calculated using X-ray diffraction. For surface roughness and to see the structure of individual grains, Atomic Force Microscope (AFM) was used. Composition analysis of coated film was carried out by Energy Dispersive X-ray Spectroscopy (EDX) and the formation of grains in the coated film was obtained by Scanning Electron Microscope (SEM).

¹Corresponding author – K.V.A.N.P.S. Kumar
2. Substrate Preparation Methods

Ti-Zr-V films were deposited on stainless steel, aluminium and glass substrates. The typical dimensions were 10X10X2 mm for metal substrates and 50X25X2 mm for glass substrates. The metal substrates were used for X-ray ray diffraction (XRD), microstructure, and compositional studies while glass substrate was used for surface roughness measurement by AFM. Prior to loading in the coating chamber, all the substrates were chemically and ultrasonically cleaned. Titanium (Ti), Zirconium (Zr), Vanadium (V) wires were twisted and placed coaxially in a cylindrical vacuum chamber connected to a DC Power Supply (Parameters: - 1kV and 1A). To study wall thickness uniformity, substrates were placed at different positions of the chamber. The detail of the coating procedure is explained elsewhere [1]. The details of Ti-Zr-V target preparation and other parameters are given in Table 1.

Table-1: Details of Ti-Zr-V target preparation, deposition parameters and its composition.

| Target Wire ratio (Ti:Zr:V) | Substrate belongs to | Deposition Parameters (Discharge Voltage, Discharge Current, Argon gas Pressure, Magnetic Field, Temperature of substrate) | Ti-Zr-V Composition | Thickness of coated film on substrate (µm) |
|-----------------------------|----------------------|-------------------------------------------------------------------------------------------------|----------------------|------------------------------------------|
| 1:2:2                       | Chamber_D            | -600V, 150 mA, 1.3X10^{-2} mbar, 250 Gauss, 150°C                                              | Ti-25%, Zr-27%, V-48% | 1.65                                     |
| 2:2:1                       | Chamber_LA           | -600V, 200 mA, 2.5X10^{-2} mbar, 220 Gauss, 150°C                                              | Ti-59%, Zr-16%, V-25% | 3.6                                      |
| 2:2:1                       | Chamber_LB           | -600V, 250 mA, 2.5X10^{-2} mbar, 220 Gauss, 150°C                                              | Ti-59%, Zr-18%, V-23% | 4                                        |

3. Characterization Studies

The analysis of surface roughness and grain formation was carried out using an AFM (AFM: SOLVER PRO, NT-MDT) on glass substrate. The compositional studies and image capture were done using SEM (PHILIPS XL30) on metal substrates. X-ray diffraction of all the substrate was carried out using Rigaku Diffractometer (GEIGERFLEX) with curved crystal graphite 224R monochromator. The XRD data was recorded at Cu-Kα in the 2θ range of 15°-70° at a step of 0.02°.

3.1. Adhesion

In order to perform coatings satisfactorily, they must adhere to the substrates on which they are applied. The scotch tape test was used to test the adhesion of the coating on the chamber wall. One coated chamber (which was activated several times at higher temperatures up to 350-450°C) was subjected for scotch tape test. The adhesion was tested as per the US Military Standard (M-13508-C). The coated film passed the test.

3.2. Morphological, structural & chemical composition analysis

Using AFM and SEM, the surface morphology of NEG films were studied. It was clear from the comparison with AFM data of National Synchrotron Light Laboratory (LNLS), Brazil [3] that the desired characteristics related to the nanometre structure of the films were met for NEG coating carried out at RRCAT.

3.2.1. Surface Roughness Studies of thin films.

The important parameter in evaluation of Ti-Zr-V NEG film is its surface roughness. The rougher the surface, larger the actual area available for pumping. With increased roughness more sites for pumping becomes available, as a result pumping speed also enhances. It also provides more multiple surface reflections and the probability that the molecule is trapped and therefore leads to gettering action. The 2D and 3D AFM images of the films are given in the figure 1 to figure 6 for all the three substrates prepared.
The observation of surface roughness found from Ti-Zr-V coated glass substrates using AFM is given in table 2.

| Substrate Belongs to | Average roughness (nm) | R.M.S. roughness (nm) | Peak to Peak roughness (nm) |
|----------------------|------------------------|-----------------------|-----------------------------|
| Chamber_D            | 2.2                    | 2.93                  | 29                          |
| Chamber_LA           | 10.9                   | 13.6                  | 103                         |
| Chamber_LB           | 21.0                   | 26.0                  | 168                         |

The AFM results of Ti-Zr-V film from UHVTD are comparable to that of LNLS, Brazil [3]. The observed peak roughness of the films deposited at LNLS is of 80 nm. Also, the LNLS film had less uniform grains indicating larger roughness, smaller grain size, and larger surface area. These characteristics are very interesting for NEG application. The observations obtained from films coated of RRCAT are in agreement with the observations given by LNLS group [3]. The measured pumping
speed of 0.7 l/s/cm² for H₂ found with the Ti-Zr-V film deposited on Chamber_D using a pumping speed setup [2].

3.2.2. X-ray Diffraction Analysis.
The X-ray diffraction pattern of Ti-Zr-V film coated over stainless steel (SS) substrate and glass are shown in figure 7 and figure 8. A diffraction peak due to film was observed near 2θ≈38.3° for both the substrates. Two substrate related peaks were also observed for the film coated over SS. The observed peak can be indexed with (002) peak of titanium (JCPDS 05-682). The crystallite size (d) was calculated using Debye Scherer relation:

\[ d = \frac{0.9 \lambda}{\Delta \cos \theta} \]

Here \( \lambda \) is the wavelength used i.e. 0.15418nm for Cu-Kα, \( \Delta \) is FWHM of diffraction peak, \( \theta \) is the angular position of recorded peak in radians. The instrumental broadening was calculated by carrying out X-ray diffraction on silicon powder. The data was corrected for instrumental broadening before calculating the crystallite size. The calculated crystallite size for films deposited over SS substrate is 14 nm.

![Fig. 7. XRD pattern for TiZrV coated film on Stainless Steel substrate of Chamber_LB](image1)

![Fig. 8. XRD pattern for TiZrV coated film on Glass Substrate of Chamber_LB](image2)

3.2.3. SEM/EDX Studies.
Images of the surface of the films were obtained in a XL 30 Philips microscope. The grain information (in air exposed NEG sample) obtained through SEM can be seen from the figure 9. The grains are clearly visible and they are in conical form. This implies that the grain formation found to be uniform throughout the region of film and uniform in shape. The arrangement of grains of chamber_LB was in agreement with 2D AFM image observations as shown in figure1 to figure 3. The composition details are given as ternary diagram in figure 10.
3.2.4. Vacuum characterization of NEG coated chambers.

Ti-Zr-V non evaporable getter coatings help in achieving ultra high vacuum of the order of $10^{-11}$ mbar and below. Their presence acts as barrier for hydrogen even in unbaked systems. Reduction in hydrogen partial pressure by three orders was observed in the present study. The figure 11 shows the details of residual gas present in vacuum chamber under different conditions. Trapped argon gas content was found during the activation studies of chamber at an elevated temperature of 300°C. The evolution of gases corresponding at 300°C was shown in figure 11. The order of gas release observed was as follows Hydrogen (H$_2$), Methane (CH$_4$), Argon (Ar) followed by CO, H$_2$O and CO$_2$. This behaviour was as expected in an ultra high vacuum environment.

![Fig. 9. SEM Micrograph of Chamber_LB](image1)

![Fig. 10. Composition in Ternary diagram](image2)

![Fig. 11. Details of gas evolution and barrier effect of NEG coated vacuum chambers.](image3)
4. Conclusion
The characterization of Ti-Zr-V non evaporable getter coated chambers provided very encouraging results. The adhesion property of the film was good even after repeated activation of the chamber. The AFM images gave an excellent information about the surface roughness and grain information. The data obtained by SEM also confirmed that the grain formation was uniform and grains are arranged in regular manner. XRD measurements also gave an indication about the nano-crystalline formation of the film and estimation of the grain size. The trapping of the argon gas during the coating can be avoided by mild baking and prolonged pumping of the coated chamber before removing from the coating system. The ultimate vacuum of the order of 2.6X10^{-12} mbar was achieved in both chamber_LA, Chamber_LB and 1X10^{-11} mbar in the chamber_D.

Acknowledgement
The encouragement of Director, RRCAT is sincerely acknowledged. The authors would also like to acknowledge the support from all the members of UHVTD, RRCAT.

Reference
[1] Shukla S K, Sindal B K, Tripti Bansod and Kumar K V A N P S Conference Proceedings by IVS Symposium on Thin Films:Science & Technology, November 09-12, 2011, BARC, Mumbai.
[2] Tripti Bansod, Sindal B K, Kumar K V A N P S and Shukla S K Conference Proceedings by IVS Symposium on Thin Films: Science & Technology, November 09-12, 2011, BARC, Mumbai.
[3] Marcelo J. Ferreira, Denise A, Tallarico, Pedro A.P.Nascente AIP conference Proceedings 1092, 168 (2009) (Synchrotron Radiation in Materials Science:6th International Conference, edited by R. Magalhaes-Panigo 168-172 2009).