Non-Evaporable Getter (NEG) Coating Using Titanium and Palladium Vacuum Sublimation

Tetsuya MIYAZAWA^{1,*}, Kensuke TOBISHIMA², Hiroo KATO², Masashi KURIHARA³,

Shinya OHNO³, Takashi KIKUCHI⁴ and Kazuhiko MASE^{1, 4}

¹SOKENDAI, Tsukuba, Ibaraki 305–0801, Japan

²Hirosaki University, Hirosaki, Aomori 036–8561, Japan

³Yokohama National University, Yokohama, Kanagawa 240–8501, Japan

⁴KEK, Tsukuba, Ibaraki 305–0801, Japan

(Received November 15, 2017 ; Accepted January 31, 2018)

We have developed a new non-evaporable getter (NEG) coating using titanium and palladium vacuum sublimation. The inner wall of the test chamber was coated with a 1- μm Ti thin film using the Ti sublimation pumps under a vacuum of 6.5×10^{-6} Pa (Ti-coated chamber). This chamber was then coated with a 10-nm Pd thin film using the Pd sublimation filament under a vacuum of 2.4×10^{-4} Pa (Pd/Ti-coated chamber). The uncoated, Ti-coated, and Pd/Ti-coated chambers were baked for 6 h at a maximum temperature of 185°C. Five hours after closing the valve, the pressures in the Pd/Ti-coated chamber were about 1.4×10^{-6} Pa even after six heating–venting cycles. The relatively low activation temperature was attributed to the low concentration of oxygen in the Pd/Ti thin films. The Pd/Ti coating can be used for vacuum systems that are frequently vented.

KEYWORDS : non-evaporable getter, vacuum, titanium, palladium, thin film

1. Introduction

Non-evaporable getter (NEG) pumps are widely used in ultrahigh vacuum (UHV) technology because they have a high pumping speed for active residual gases (especially hydrogen) and are oil-free, vibration-free, energy-saving, magnetic-field-free, compact, and lightweight components.^{1–3)} NEG thin films that can be activated by *in situ* baking are more useful for accelerators because high pumping speeds can be achieved without requiring any additional space and because outgassing from chambers can be suppressed.^{4, 5)} In the framework of the Large Hadron Collider (LHC) project, work to produce NEG thin films based on sputtering techniques was started at the end of 1995 at CERN⁶⁾. Ti-Zr thin films sputtered on vacuum chambers are activated by heating at 200–

250°C,^{5, 6)} and Benvenuti *et al.*^{6, 7)} found that sputter-deposited thin films of Ti-Zr-V can be fully activated after 24 h of *in situ* heating at 180°C. The Ti-Zr-V sputter coating technology was applied to the vacuum chamber for the European Synchrotron Radiation Facility (ESRF) in 2000⁸⁾ and is now widely used in particle accelerators and synchrotron light sources all over the world. Recently, Malyshev *et al.*⁹⁾ reported that sputter-deposited thin films of Ti-Zr-Hf-V can be activated at a lower temperature of 150–160°C after baking for 24 h.

However, the probability of H₂ sticking on a sputter-coated Ti-Zr-V film after activation at 200°C was found to decrease rapidly after repeated heating–venting cycles.⁶⁾ Heating–venting cycles result in progressive oxygen enrichment of the Ti-Zr-V film, which in turn limits its operating life.¹⁰⁾ To overcome this, Benvenuti *et al.*^{10, 11)} proposed the use of a magnetron-sputtered Pd thin film coating on the

*E-mail : miyazate@post.kek.jp

NEG thin films. A similar idea was presented in a previous patent in 1995 by Tsuji and Takeuchi,¹²⁾ in which Ti coated with a Pd thin film was proposed as a vacuum material. Since the energies for hydrogen surface adsorption and bulk dissolution are -0.53 and -0.1 eV, respectively, for Pd and -0.92 and -0.47 eV, respectively, for Ti,¹³⁾ hydrogen adsorbs and diffuses into the NEG thin film through the Pd coating at room temperature. During activation, hydrogen desorbs from the NEG film, diffuses through the Pd coating, and then desorbs as H_2 into the vacuum. Thus, NEG films coated with Pd will be durable against repeated heating–venting cycles. However, to the best of our knowledge, there is little experimental evidence for Pd coatings improving the operating life of NEG thin films. Experimental difficulty in preparing Pd-coated NEG thin film seems to exist in suppressing oxides at the Pd/NEG interface because an oxide layer, such as TiO_2 , works as an efficient hydrogen barrier.

In the present paper, we report a new method for manufacturing Ti and Pd/Ti thin films with a low oxygen concentration using vacuum sublimation. When the deposition rate of Ti is much larger than the impingement rate of residual oxygen-containing molecules, the oxygen concentration in the Ti film will be negligible. In the sputter deposition method, it is difficult to reduce the amount of oxygen-containing gases released with the sputtering, whereas in the vacuum sublimation method, the amount of oxygen-containing gas can be reduced easily by reducing the pressure during sublimation. The inner walls of a test chamber were coated with a $1\text{-}\mu\text{m}$ -thick Ti film under a pressure of 6.5×10^{-6} Pa using vacuum sublimation (Ti-coated chamber). The Ti-coated chamber was then coated with a 10-nm -thick Pd film under a pressure of 2.4×10^{-4} Pa using vacuum sublimation (Pd/Ti-coated chamber). The Ti-coated and Pd/Ti-coated chambers were found to work as NEG pumps after a 6-h bake at a maximum temperature of 185°C . Furthermore, the pumping speed of the Pd/Ti thin-film coating did not degrade even after two heating–dry- N_2 -venting, two heating–dry-air-venting, and two heating–air-venting cycles. The present NEG coating will open up new applications in vacuum-related industries.

Fig. 1. (color online). Schematic of the experimental apparatus. The test chamber is pumped with a turbomolecular pump via a butterfly valve. Two Ti sublimation pumps are installed for Ti vacuum sublimation, one of which is replaced with a Pd sublimation filament for Pd vacuum sublimation. The total pressure is measured with a B-A nude ionization gauge. A vent port with a heat exchange tube is installed. For dry N_2 or dry air vent the heat exchange was dipped in liquid N_2 .

2. Experimental

The apparatus used for the experiments consisted of a test chamber, a manual butterfly valve (VAT, 20040-CE04), a 300-L s^{-1} turbomolecular pump (TMP ; Edwards, STP301), two Ti sublimation pumps (TSPs ; Canon Anelva, tie-back pump, 956-7040), Bayard Alpert (B-A) nude ionization gauge (Canon Anelva, NIG-2F), and a vent port as shown in **Fig. 1**. The test chamber is made of stainless steel 304L (SS304L) with two DN 160 ConFlat® flanges (CFs), two DN 100 CFs, thirteen DN 40 CFs, and four DN 16 CFs. The inner walls of the chamber are electropolished, and the total inner surface area is about 4300 cm^2 . The TMP is backed by a 50-L s^{-1} TMP, a foreline trap, and an oil rotary pump (RP). In the case of the Pd vacuum sublimation, a Pd sublimation filament is attached instead of the Ti sublimation pump. The Pd filament is made of two twisted 0.8-mm -diameter Pd wires with a purity of 99.95% (Nilaco, PD-341465). The B-A gauge is attached to the end of a long DN 40 CF elbow to avoid deposition of Ti and Pd. The temperature of the outer wall of the underside of the test chamber was measured with a K-type thermocouple. The test chamber can be baked using a sheath heater and three tape heaters with a maximum temperature of 185°C ,

while the butterfly valve can be baked with a sheath heater for the same period with a maximum temperature of 130°C. When the chamber was vented with dry N₂ or dry air, the heat exchange tube of the vent port was dipped in liquid N₂ to suppress water vapor contamination. The Pd filament was not equipped under Ti sublimation to avoid Ti deposition on the Pd filament during this test.

The Ti thin film was coated using the following procedure. The uncoated test chamber after four dry-N₂-venting-pumpdown-baking-cooling circles was pumped and baked for 12 h at a maximum temperature of 185°C. After cooling to room temperature, the total pressure reached 4.8×10^{-8} Pa. The two TSPs were then operated at 48 A for 3 h in turn (6 h in total). According to the TSP manual, the Ti sublimation rate is 0.35 g h⁻¹ at 48 A. Thus the mass of the sublimated Ti was 2.1 g. The pressure under Ti sublimation was 6.5×10^{-6} Pa. Since the total inner wall area of the test chamber is about 4300 cm², the average thickness of the Ti thin film was estimated to be 1 µm.

The Pd thin film was then coated as follows. The test chamber was vented with dry N₂, and one of the TSPs was replaced with the Pd sublimation filament while purging dry N₂ to suppress introduction of H₂O and O₂. The Pd filament was not equipped under Ti sublimation to avoid Ti deposition on the Pd filament during the previous test. The Ti-coated chamber was pumped and baked for 12 h at a maximum temperature of 185°C. During the baking, the Pd sublimation filament was heated using a current of 10 A to degas. After cooling to room temperature, the total pressure reached 6.0×10^{-8} Pa. The Pd filament was then sublimated at 21.7 A under a pressure of 2.4×10^{-4} Pa. The Pd thin film was deposited at a rate of 0.1 Å/s for 1,000 s. The rate of Pd sublimation was confirmed in advance using a thin film rate/thickness monitor (STM-2, Inficon). The average thickness of the Pd thin film on the inner walls of the test chamber was estimated to be about 10 nm. The Pd thickness is not uniform because the thickness depends on the distance between the chamber-wall and the Pd filament, and on the evaporation angle.

The pumpdown curves of the uncoated, Ti-coated, and Pd/Ti-coated test chamber were measured by venting the test chamber to atmospheric pressure by

using dry N₂, dry air, or air. The RP, 50-L s⁻¹ TMP, and 300-L s⁻¹ TMP started pumping in this order, and 1 h after the 300-L s⁻¹ TMP entered normal operation, the total pressure of the test chamber was measured using the B-A gauge. Two hours after the 300-L s⁻¹ TMP entered normal operation, the test chamber was baked for 6 h at a maximum temperature of 185°C. After baking, the test chamber was cooled to room temperature. Twenty hours after the 300-L s⁻¹ TMP went into normal operation, the manual butterfly valve between the test chamber and the TMPs was closed. The pressure curves were measured for 5 h after the butterfly valve was closed.

3. Results

Fig. 2 shows the pumpdown curves and temperature of the uncoated test chamber after an air or dry N₂ vent. The total pressure was measured with the B-A gauge at the end of a DN 40 CF elbow (see Fig. 1). The total pressure after the air vent was 10–3 times larger than that after the dry N₂ vent. The results indicate that water adsorption on the inner walls of the SS304 chamber increased the pressure even after a 6-h bake. In the case of the fourth dry N₂ vent, the total pressure reached 1×10^{-6} Pa two hours after the TMP entered normal operation. When the baking started, the pressure jumped to 1×10^{-5} Pa and gradually decreased to 4×10^{-6} Pa within a one and a half hour. The

Fig. 2. (color online). Pumpdown curves and typical temperature of the uncoated test chamber for the first, second, third, and fourth venting-pumpdown-baking-cooling cycles. The pumpdown curve after air venting, pumpdown, baking, and cooling is also shown for comparison. The time when the 300-L s⁻¹ TMP enters normal operation is taken as the origin of the time axis.

Fig. 3. Pressure curve of the uncoated chamber after closing the butterfly valve at a pressure of 3×10^{-8} Pa in the case of the dry N_2 vent. The time the butterfly valve is closed is taken as the origin of the time axis.

pressure then increased to 1.5×10^{-5} Pa as the temperature of the chamber increased to 185°C . When the baking was finished, the pressure decrease followed the temperature decrease.

Fig. 3 shows the pressure curve of the uncoated chamber after closing the butterfly valve at a pressure of 3×10^{-8} Pa in the case of the dry N_2 vent. When the valve was closed, the pressure jumped to 1×10^{-5} Pa and gradually increased to 1×10^{-4} Pa in four and half hours. Outgassing from the viton O-ring of the butterfly valve is thought to be responsible for the pressure jump to 1×10^{-5} Pa. The results indicate that the electropolished SS304 surface does not work as a NEG pump.

Fig. 4 shows the pumpdown curves and temperature of the Ti-coated chamber after the dry N_2 vent. After the Ti sublimation, the Ti-coated chamber was baked for 6 h at a maximum temperature of 185°C and cooled to room temperature. The second venting–pumpdown–baking–cooling cycle was carried out in the same way. The pressure of the Ti-coated chamber jumped to $(1\text{--}5) \times 10^{-4}$ Pa just after baking started. These pressures are 10–50 times higher than those of the uncoated chamber, and the results indicate that outgassing from the Ti-coated chamber is 10–50 times larger than that of the uncoated chamber in the initial pumpdown stage. The pressure monotonically decreased while the temperature of the chamber increased, and the pressure of the Ti-coated chamber after baking decreased more

Fig. 4. (color online). Pumpdown curves and typical temperature of the Ti-coated chamber after the first and second venting–pumpdown–baking–cooling cycles. The pumpdown curve of the uncoated chamber after the fourth dry N_2 vent is shown for comparison.

Fig. 5. (color online). Pressure curves of the Ti-coated chamber after closing the butterfly valve at a pressure of 4×10^{-8} Pa after the first and second venting–pumpdown–baking–cooling cycles. The pressure jump just after the valve closed was different each time, suggesting that the amount of outgassing from the valve depends on the handling when closing the valve. The pressure curve of the uncoated chamber after the fourth dry N_2 vent is shown for comparison.

rapidly than that of the uncoated chamber. The time required to reach 1×10^{-7} Pa was about one hour shorter in the case of the Ti-coated chamber.

Fig. 5 shows the pressure curves of the Ti-coated chamber after closing the butterfly valve at a pressure of 4×10^{-8} Pa in the case of the dry N_2 vent. In the first cycle, the pressure of the Ti-coated chamber jumped to 1×10^{-6} Pa when the valve is closed and then decreased to 2.2×10^{-7} Pa in 5 h. This indicates

Fig. 6. (color online). Pumpdown curves and typical temperature of the Pd/Ti-coated chamber after the first, second, third, fourth, fifth, and sixth venting–pumpdown–baking–cooling cycles. Dry N₂, dry air, and air were used in the first and second, third and fourth, and fifth and sixth venting cycles, respectively. The pumpdown curves of the uncoated chamber after the air vent and fourth dry N₂ vent are shown for comparison. The pumpdown curve for the 5th cycle in the period of 8–10 h is disturbed due to the misoperation of the bakeoff.

that the Ti-coated chamber works as a NEG pump. In the second cycle, the pressure jumped to 5×10^{-3} Pa but then decreased to 1×10^{-6} Pa in 5 h, indicating that the Ti-coated chamber works as a NEG pump even after two venting–pumpdown–baking–cooling cycles.

Fig. 6 shows the pumpdown curves and temperature of the Pd/Ti-coated chamber after the first, second, third, fourth, fifth, and sixth venting–pumpdown–baking–cooling cycles. Dry N₂, dry air, and air were used in the first and second, third and fourth, and fifth and sixth venting cycles, respectively. After baking in the case of the dry N₂ vent, the pressure decreased more rapidly than that of the uncoated chamber, and the time required to reach 1×10^{-7} Pa was about one and a half hours shorter.

Fig. 7 shows the pressure curves of the Pd/Ti-coated chamber after closing the butterfly valve at a pressure of 4×10^{-8} Pa after the first, second, third, fourth, fifth, and sixth cycles. The pressure jump just after the valve closed was different each time, suggesting that the amount of outgassing from the valve depends on the handling when closing the valve. The pressure five hours after the valve was closed was about 1×10^{-6} Pa. These results indicate that the Pd/Ti-coated chamber works as a NEG pump after a 6-h

Fig. 7. (color online). Pressure curves of the Pd/Ti-coated chamber after closing the butterfly valve in the range of 10^{-8} Pa after first, second, third, fourth, fifth, and sixth venting–pumpdown–baking–cooling cycles. Dry N₂, dry air, and air were used in the first and second, third and fourth, and fifth and sixth vent cycles, respectively. The pressure jump just after the valve closed was different each time, suggesting that the amount of outgassing from the valve depends on the handling when closing the valve. The pressure curve of the uncoated chamber in the case of the fourth dry N₂ vent is shown for comparison.

bake at a maximum temperature of 185°C even after six venting–pumpdown–baking–cooling cycles.

4. Discussion

Since the pressure P is given by

$$P = \frac{Q}{S}$$

where Q is the total outgassing rate and S is the pumping speed, the pressures before and after closing the butterfly valve ($P_{t=0}$ and $P_{t=5}$) are approximately $P_{t=0} \approx \frac{Q_{t=0}}{S_{\text{TMP}} + S_{\text{NEG}}}$ and $P_{t=5} \approx \frac{Q_{t=5}}{S_{\text{NEG}}}$, respectively, where $Q_{t=0}$ and $Q_{t=5}$ are the total outgassing rates when the butterfly valve is open and closed, respectively (see Figs. 5 and 7). Here, t represents the time in hours after the butterfly valve was closed. Because the outgassing rates per unit area of H₂, H₂O, CO, and CO₂ from SS316L are reported to be 17, 0.74, 0.37, and 0.17×10^{-7} Pa L m⁻² s⁻¹, respectively, after a 20-h bake at 150°C,¹⁴⁾ we assumed that the residual gas is solely H₂. Assuming that $Q_{t=0} = Q_{t=5}$ the pumping speed of the NEG (Ti or Pd/Ti) thin film S_{NEG} is roughly estimated from the following equation,

Fig. 8. (color online). Variation of the estimated H_2 pumping speed for Ti and Pd/Ti thin films as a function of the number of heating-venting cycles. $P_{t=-0.25}$ was used instead of $P_{t=0}$ in the estimation of S_{NEG} of the Ti thin film for the second cycle.

$$S_{\text{NEG}} = \frac{P_{t=0}}{P_{t=5} - P_{t=0}} S_{\text{TMP}},$$

where S_{TMP} is the pumping speed of the TMP for H_2 . According to the STP-301 TMP manual, S_{TMP} is 300 L s^{-1} for H_2 . **Fig. 8** shows estimated S_{NEG} as a function of the number of heating-venting cycles for the Ti and Pd/Ti thin films. In the case of the Ti thin film, S_{NEG} was 67 L s^{-1} for the first heating-venting cycle but reduced to 13 L s^{-1} for the second cycle. This is reasonable because the Ti surface is oxidized by H_2O and/or O_2 above room temperature.¹⁵⁾ The oxides on clean Ti surface can be removed by heating to about 850 K .¹⁵⁾ In contrast, in the case of the Pd/Ti thin film, estimated S_{NEG} was in the range of $9\text{--}21 \text{ L s}^{-1}$ over the six heating-venting cycles. These results show that the Pd/Ti thin film is durable against heating-venting cycles. The Pd coating seems to prevent Ti from being oxidized during six heating-venting cycles. The results are also reasonable because Pd is not oxidized at room temperature.¹⁶⁾ The smaller estimated S_{NEG} of the Pd/Ti thin film suggests that the Ti layers at the Pd/Ti interface are more oxidized than the surface of the Ti thin film. The oxidation of the Pd/Ti interface seems to proceed during the dry N_2 venting before the Pd vacuum sublimation and during Pd sublimation under a relatively high pressure of $2.4 \times 10^{-4} \text{ Pa}$. The oxides at the Pd/Ti interface are expected to be suppressed if Ti and Pd sublimation are carried out without breaking vacuum in the pressure range of 10^{-7}

Pa. For this purpose a Ti and Pd evaporator which consists of a Ti filament, a Pd filament, shield plates, and an electric feedthrough is now under construction.

The lowest measured activation temperature for the Ti thin film coated with the sputtering method developed by Benvenuti *et al.* was reported to be about 200°C for a 24-h bake.⁴⁾ In contrast, the activation conditions for the present Ti and Pd/Ti thin films coated using vacuum sublimation is a 6-h bake at a maximum temperature of 185°C (see Figs. 4 and 6). The difference in the activation temperature seems to be derived from the concentration of oxygen in the Ti thin film. Since Ti is thought to be oxidized by H_2O under UHV conditions, the concentration of oxygen (c_{O}) in the Ti thin film coated using vacuum sublimation is given by the following equation,

$$\begin{aligned} c_{\text{O}} &\approx \frac{\Gamma_{\text{H}_2\text{O}} \times s_{\text{H}_2\text{O}}}{\Gamma_{\text{Ti}}} = \frac{p_{\text{H}_2\text{O}}}{\sqrt{2\pi m_{\text{H}_2\text{O}} kT}} \times \frac{s_{\text{H}_2\text{O}}}{\Gamma_{\text{Ti}}} \\ &= \frac{p_{\text{H}_2\text{O}}}{\sqrt{2\pi m_{\text{H}_2\text{O}} kT}} \\ &\quad \times \frac{s_{\text{H}_2\text{O}} \times t_{\text{sub}} \times A}{N_{\text{Ti}}} \end{aligned}$$

where $\Gamma_{\text{H}_2\text{O}}$ is the impingement rate of H_2O , $s_{\text{H}_2\text{O}}$ is the initial sticking coefficient of H_2O on the Ti film, Γ_{Ti} is the impingement rate of Ti, $p_{\text{H}_2\text{O}}$ is the partial pressure of H_2O , $m_{\text{H}_2\text{O}}$ is the mass of H_2O , k is Boltzmann's constant, T is the temperature, N_{Ti} is the number of evaporated Ti atoms, t_{sub} is the sublimation time, and A is the total inner surface area of the test chamber. As stated above, the outgassing rates per unit area of H_2 , H_2O , CO , and CO_2 from SS316L are reported to be 17, 0.74, 0.37, and $0.17 \times 10^{-7} \text{ Pa L m}^{-2} \text{ s}^{-1}$, respectively, after a 20-h bake at 150°C .¹⁴⁾ Since Ti sublimation was carried out after a 12-h bake at a maximum temperature of 185°C , the percentage of H_2O in the total residual gas is thought to be less than 5%. Assuming that the residual gasses were composed of 95% H_2 and 5% H_2O , $p_{\text{H}_2\text{O}}$ is estimated to be $7.5 \times 10^{-7} \text{ Pa}$ because the relative sensitivities to N_2 of the B-A ionization gauges are 0.44 and 1.0 for H_2 and H_2O according to the B-A gauge manual. Thus, $\Gamma_{\text{H}_2\text{O}}$ is less than $2.7 \times 10^{16} \text{ molecules s}^{-1} \text{ m}^{-2}$. One report¹⁷⁾ gives $s_{\text{H}_2\text{O}}$ as 0.5, and in the present case, Γ_{Ti} is about $3 \times 10^{18} \text{ atoms s}^{-1} \text{ m}^{-2}$ because the Ti sublimation rate was 0.35 g h^{-1} , and A is about 4300 cm^2 . From these

Fig. 9. (color online). Schematics of the proposed activation and pumping mechanisms of the (a) Ti thin film coating using conventional dc magnetron sputtering, (b) ideal oxygen-free Ti thin film coating using vacuum sublimation, and (c) ideal oxygen-free Pd/Ti thin film coating using vacuum sublimation.

values, c_0 is thought to be less than 0.5%.

In the case of the dc magnetron sputtering method, it is difficult to estimate the atomic percentage of oxygen from the pressure because oxygen-containing gasses are supplied by the sputtered walls and rare gas inlet. In an X-ray photoelectron spectroscopy (XPS) study of Ti–Zr–V thin films prepared with the dc magnetron sputtering method, Šutara *et al.*¹⁸⁾ reported that the air-exposed (as-received) Ti–Zr–V surface is covered by an oxide layer such as TiO₂ and ZrO₂. According to another XPS study by Jeyachandran *et al.*,¹⁹⁾ the atomic percentage of oxygen in the Ti thin film deposited by dc magnetron sputtering is 67–82% for a base vacuum of $(4\text{--}13) \times 10^{-4}$ Pa. Therefore, the activation temperature of the sputtered NEG film is limited by the activation energy of the oxygen diffusion.⁸⁾ Schematics of the proposed activation and pumping mechanisms of the Ti thin film coating

using conventional dc magnetron sputtering is shown in Fig. 9(a).

In the case of an ideal oxygen-free Ti thin film prepared by Ti vacuum sublimation, the activation temperature is thought to be limited by the activation energy of hydrogen diffusion. After venting at room temperature, the Ti surface is oxidized by H₂O and/or O₂.¹⁵⁾ Because the oxide layer is not reduced even at 650 K (377°C),¹⁵⁾ the Ti thin film after baking at a maximum temperature of 185°C in the present case is thought to be covered with an ultrathin oxide layer. Hydrogen is thought to diffuse through the ultrathin oxide layer because the atomic radius of hydrogen is quite small. Schematics of the proposed activation and pumping mechanisms of the ideal oxygen-free Ti thin film coating using vacuum sublimation is shown in Fig. 9(b). Repeated heating–venting cycles result in a progressive oxygen enrichment of the Ti thin film,

which in turn reduces its pumping speed.¹⁰⁾

The atomic percentage of oxygen in the Pd thin film is thought to be negligible because H₂O does not adsorb on the Pd surface at room temperature.²⁰⁾ In the case of an ideal oxygen-free Pd/Ti thin film, the activation temperature is also thought to be limited by the activation energy of hydrogen diffusion as shown in Fig. 9(c). According to a previous study,¹⁶⁾ the Pd(111) surface at room temperature is covered with a 1/4 monolayer of oxygen.

Schematics of the proposed activation and pumping mechanisms of the ideal oxygen-free Pd/Ti thin film coating using vacuum sublimation is shown in Fig. 9(c).

The pressure of the Ti-coated chamber before baking was about one order of magnitude higher than that of the uncoated chamber (see Fig. 4), while that of the Pd/Ti-coated chamber before baking was about one and a half orders of magnitude higher (see Fig. 6). These results suggest that hydrogen gases absorbed in the Ti or Pd/Ti thin films increased the outgassing rate before baking.

The pressure five hours after the valve was closed was about 2.2×10^{-7} Pa for the Ti-coated chamber (see Fig. 5), and about 1×10^{-6} Pa for the Pd/Ti-coated chamber (see Fig. 7). Since the pressure is proportional to the total outgassing rate, the ultimate pressure is expected to be improved when the baking time is increased.

5. Conclusion

We have developed a new NEG coating method using vacuum sublimation of Ti and Pd. The inner walls of the test chamber were coated with a 1- μ m Ti thin film using Ti sublimation pumps under a vacuum of 6.5×10^{-6} Pa (Ti-coated chamber). The Ti-coated chamber was then coated with a 10-nm Pd thin film using a Pd sublimation filament under a vacuum of 2.4×10^{-4} Pa (Pd/Ti-coated chamber). The uncoated, Ti-coated, Pd/Ti-coated chambers were activated by baking for 6 h at a maximum temperature of 185°C. The pressure in the Ti- and Pd/Ti-coated chambers after baking decreased more rapidly than that in the uncoated chamber. The pressures in the Ti-coated chamber after the first and second venting–pump-down–baking–cooling cycles decreased to about

2×10^{-7} and 1×10^{-6} Pa, respectively, after the butterfly valve between the chamber and the TMP was closed. The pressure in the Pd/Ti-coated chamber after six venting–pumpdown–baking–cooling cycles decreased to about 1×10^{-6} Pa after the butterfly valve was closed. These results indicate that the Ti- and Pd/Ti-coated chambers work as NEG pumps after baking for 6 h at a maximum temperature of 185°C even after repeated heating–venting cycles. The pumping speeds of the Ti thin film for H₂ were roughly estimated to be 67 and 13 L s^{−1} after the first and second cycles, respectively. In the case of the Pd/Ti thin film, the pumping speed was roughly estimated to be in the range of 21–9 L s^{−1} from the first to sixth heating–venting cycles. These results indicate that the Pd/Ti thin film is durable against repeated heating–venting cycles. The pumping speed is expected to be improved if the oxides at the Pd/Ti interface are removed.

The relatively low activation temperature of 185°C was attributed to the low concentration of oxygen (*c*_O) in the Ti and Pd/Ti thin films, where *c*_O was estimated to be less than 0.5%. Therefore, the activation temperature is thought to be limited by hydrogen diffusion and desorption in the Ti and Pd/Ti thin films. The activation temperature can be decreased because the energies of hydrogen adsorption and bulk dissolution are reported to be −0.53 and −0.1 eV, respectively, for Pd and −0.92 and −0.47 eV, respectively, for Ti.¹³⁾ The present Ti and Pd/Ti coating methods will open up new applications in which vacuum systems are frequently vented.²¹⁾

Acknowledgments

This study was supported by a Grant-in-Aid for scientific research (JSPS KAKENHI Grant Number JP26390070). The authors are grateful to Prof. Y. Tanimoto (KEK-PF), Mr. A. Toyoshima (KEK-PF), Mr. H. Tanaka (KEK-PF), Mr. H. Nishiguchi (Baroque International Inc.), and Ms. E. Kazama (Baroque International Inc.) for their invaluable advice and support.

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