富山大学水素同位体機能研究センター研究報告10・11：43−57, 1991.

論　文

未処理の真空材料に対する トリチウムの吸着

三　宅　　均・松　山　政　夫・芦　田　　完

渡　辺　国　昭・Donald F. Cowgill*

富山大学水素同位体機能研究センター
〒930 富山市五福3190

Tritium Ad/absorption for Some Vacuum Component Materials Having Non - Cleaned Surfaces

Hitoshi MIYAKE, Masao MATSUYAMA,
Kan ASHIDA, Kuniaki WATANABE
and Donald F. COWGILL*

Hydrogen Isotope Research Center, Toyama University
Gofuku 3190, Toyama 930, Japan
* Tritium Research Laboratory, Sandia National Laboratories
Livermore, California 94550, USA
(Received July 31, 1991 ; accepted October 31, 1991)

Abstract

A simple system using tritium counting and thermal desorption techniques was developed to measure tritium adsorption and/or absorptin on/in materials having non-cleaned surfaces and to estimate the tritium inventory/contamination of materials near typical conditions. The samples comprised the materials used for conventional vacuum systems.

Ad/absorbed tritium could be detected as RD(room temperature desorption), SR (surface residuum) and HD(high temperature desorption) species. With respect to organic polymers, only HT molecules dissolved in the samples were responsible for the RD,

SR and HD. As for other materials, however, the RD species was revealed to be physically adsorbed HTO. The HD species formed a peak at about 460 K for each material except organic polymers. It appeared to be adsorbed tritium, but desorbed as a condensable gas at liquid nitrogen temperature. It was, however, not soluble in water. Its chemical forms and formation mechanisms were left as open question. The SR species appeard to be a part of HD.

The order of adsorption amounts was as follows : [Epoxy resin, FRP(Fiber reinforced plastics] > [Ni(Nickel)] > [Cr(Chromium), Fe(Iron), SS304(Stainless steel), A2219(Aluminum alloy)] > [h-BN(Boron nitride), SiC(Silicon carbide), ASS(SS304 passivated by anodic oxidation layers), BSS(SS304 passivated by h-BN segregation layers]. This order was considerably different from that observed for clean surfaces. In addition, the adsorption amounts for metals/alloys were about two orders of magnitude smaller than those reported for clean metal surfaces. This discrepancy in results is apparently due to the presence of oxides and contamination layers over the samples used. Nevertheless, it was found that the passivation of SS304 with anodic oxidation and/or h-BN segregation layers should be quite valid to decrease the tritium inventory and/or contamination on/of the material walls of tritium handling systems.

1. Introduction

An appreciable tritium permeation has been estimated for the inner walls of tritium handling systems of thermonuclear fusion reactors[1]. It should be also kept in mind that replacing the tritium contaminated components with new ones is one of the most significant sources of the tritium release to environment[2]. This is also a common experience for the users of tritium facilities, Those problems require the reduction of tritium adsorption and/or absorption on/in material surfaces as low as possible from the saftey and environmental aspects.

Adsorption and/or absorption of hydrogen have already been extensively studied so far for a variety of metals, alloys, oxides and others[3]. Investigations on the ad/absorption of tritium, however, are still of great importance because the data accumulated so far are principally for clean surfaces and hence not necessarily valid for estimating, before hand, the tritium contamination and/or inventory for selected component materials having non-cleaned surfaces. In addition, there is much need of such materials being inactive to tritium ad/absorption, to decrease the tritium contamination/inventory/permeation.

We developed a simple system using tritium counting and thermal desorption tech-

niques to determine the ad/absorption activity of a given material having the surface near practical conditions; namely, as-received samples with no surface cleaning[4]. Data obtained would be valid for estimating tritium inventory on/in the walls of selected materials for the tritium handling systems.

This paper will describe the adsorption and desorption behavior of tritium ad/absorbed in various materials used for conventional vacuum systems and/or tritium handling ones. It will also refer to the differences in the material activites to tritium ad/absorption.

2. Experimental

2. 1. Apparatus

Figure 1 shows schematic diagram of the experimental apparatus used in the present study. This system consists of a tritium exposure subsystem connected to a conventional vacuum unit and counting subsystem. The tritium exposure subsystem, to be used to expose the samples to tritium gas, is equipped with an ionization gauge, capacitance manometer and Zr-alloy getters for tritium storage / supply / recovery. The details of the experimental system have been described elsewhere[4].

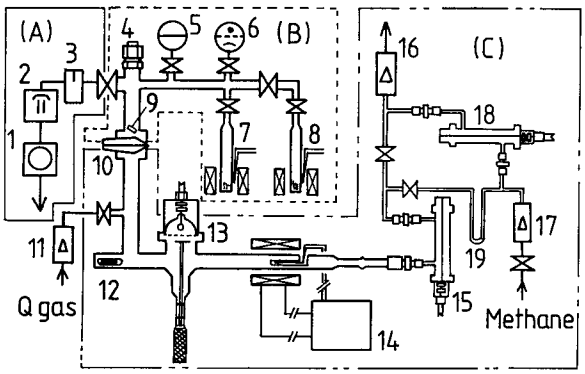


Fig. 1. Schematic apparatus installed with tritium counters and thermal desorption device.

(A) Vacuum unit : 1. oil-sealed rotary pump, 2. mercury diffusion pump, 3. cold trap, (B) Tritium exposure subsystem : 4. sample inlet, 5. capacitance manometer, 6. ionization gauge, 7.8. Zr-alloy getter, 9. sample, (C) Counting subsystem : 10. ball valve, 11.16.17. gas flow meter, 12. iron rod, 13. 2π gas flow counter, 14. programmable temperatrue controller, 15. proportional counter(PC) 1, 18. PC 2, 19. cold trap.

2. 2. Materials

The samples used were chromium(Cr), stainless steel(SS304), SS304 passivated by anodic oxidation layers(ASS) and by boron nitride segregation layers(BSS), aluminum alloy(A2219), boron nitride(h-BN), silicon carbide(SiC), epoxy resin and fiber reinforced plastics(FRP). Most of the samples were about 8×8 mm^2 with 0.3~0.5 mm thickness.

The stainless steel is one of the most conventional material to construct vacuum tight systems. The aluminum alloy could be also used for the same purpose owing to its nonsusceptible nature to hydrogen adsorption and solution. The ceramic materials, h-BN and SiC, are expected to show extremely low activities, and hence to be poten-

tial candidates as surface coating materials. Interest was also aroused to epoxy resin and FRP which are used in conventional turbomolecular pumps as a part of gap senser and motor rotor, respectively[5].

Tritium gas stored in the getter was diluted with hydrogen gas to the ratio of H/T=60. The tritium concentration was kept almost constant throughout the present study.

2. 3. Procedures

The samples were only washed with acetone before use except organic polymers. After the system being evacuated to about 1×10^{-4} Pa at room temperature, the sample was exposed to the diluted tritium gas at 4 kPa(tritium partial pressure was 67 Pa) at room temperature for 1 hour. Subsequently, the exposure gas was recovered with the getter and the system was evacuated for 1 minute. It was dropped to the counting subsystem by opening the ball valve to measure tritium adsorption and/or desorption.

The mixture gas of helium and 1% isobutane was used as carrier gas as well as quenching gas. The flow rate of the mixture gas was controlled to be 150 cm^3/min.

Desorption of tritium at room temperature was measured with the proportional counter at first. Subsequently, the sample was moved to the sample holder of the 2π counter to measure the tritium remained on the surface. Lastly, it was moved to the heatig device to measure the desorption during heating up the sample. The temperature of the sample was elevated linearly with time at heating rates of 0.08~0.33 K/sec upto 450~900 K, depending on the samples. The details of the experimental procedures have been described elsewhere[4].

3. Results and discussion

3. 1. Adsorption and/or desorption behavior

Figures 2 to 5 show some typical examples of the desorption curves and adsorption measurements with the 2π counter. As seen in the figures, the ad/absorption amounts were measured through two distinct ways. One was desorption curves observed for the sample kept at room temperature and during sample heating. The areas of those curves gave the respective desorption amounts. The other was the amount of tritium remained on/in the surface layers of the sample after the room temperature desorption. This species was measured directly by the 2π counter in between those desorption measurements. The desorption amounts at room temperature and during sample heating are

denoted as RD(room temperature desorption) and HD(high temperature desorption), respectively. The adsorbed tritium measured with the 2π counter is denoted as SR (surface residuum).

The principal features of those desorption curves were as follows: 1) A fairly large part of ad/absorbed tritium desorbed at room temperature: most of the materials showed a sharp peak, whereas organic polymers did a dull peak with long tail, 2) The residuum tritium desorbed with heating the samples, forming thermal desorption spectra, 3) Most of the desorption spectra showed a predominant peak at a temperature range of 450~480 K. 4) At high temperature side, there were a long tail

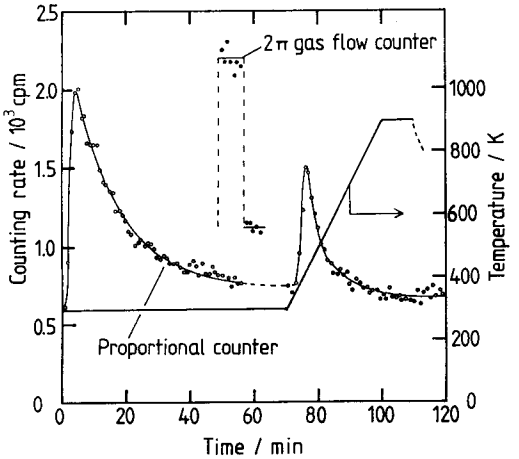


Fig. 2. Desorption curves and spectrum for SS304.

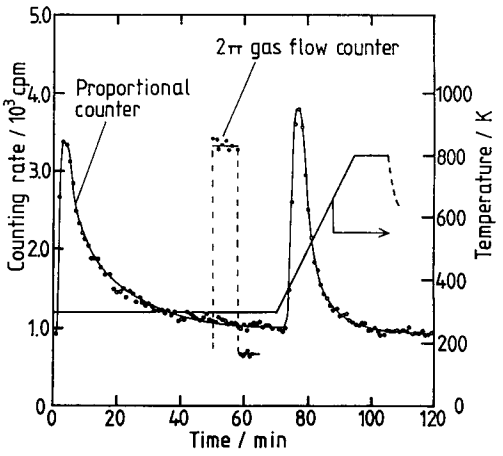


Fig. 3. Desorption curves and spectrum for A2219(aluminum alloy).

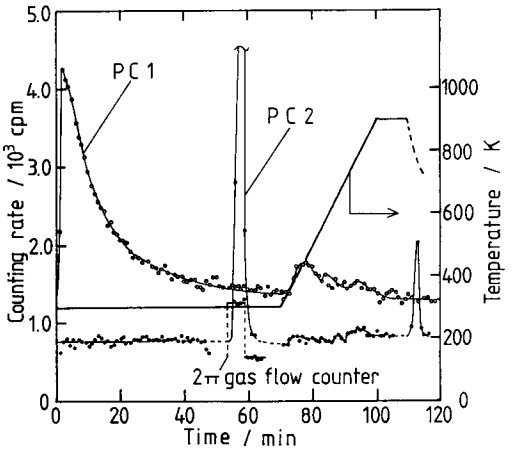


Fig. 4. Desorption curves and spectrum for SiC(Hitaceram).

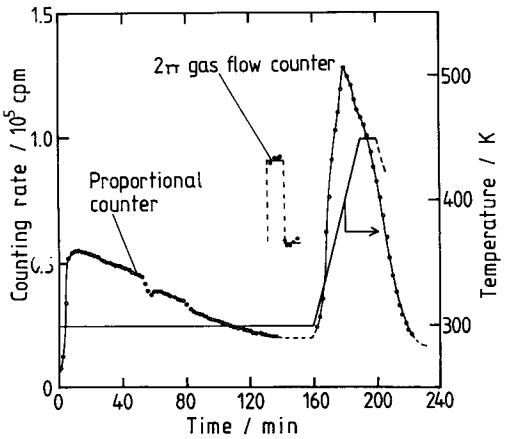


Fig. 5. Desorption curves and spectrum for FRP(fiber reinforced plastics).

and/or peaks. Those features will be discussed below.

A desorption curve (RD) or desorption spectrum (HD) through a chemical reaction is described with the equations analogous to open reactor as below[6] :

$$(dc/dt) + (S/V)c = N(t) \quad (1)$$

$$N(t) = -(d\sigma/dt) = kf(\sigma) \quad (2)$$

where c is the concentration of tritium released into the gas phase in the system of volume, V, σ the number of ad/absorbed tritium on/in the material and N(t) the rate of desorption. S and k are the flow rate of the carrier gas and rate constant for desorption, respectively. The term, $kf(\sigma)$, shows the concentration dependence of the desorption rate: for example, it is σ for the first order reaction, and σ^2 for the second order. The rate constant, k is generally written as

$$k = k_0 \exp(\Delta E_r/RT) \quad (3)$$

where k_0 is the pre-exponential factor, ΔE_r the activation energy and R the gas constant. In the case of the room temperature desorption, k was constant, whereas it varied with time for the thermal desorption spectroscopy(HD) : in the present case, the sample was heated linearly with time as $T = T_0 + \beta t$, where β is the temperature ramp. Namely, the rate constant becomes larger with time.

3. 1. 1. Metals and ceramics

3. 1. 1. 1. Room temperature desorption

It was observed that the counting rates decreased exponentially with time for the decaying parts of the room temperature desorption curves. The rate constants, k, were in the range of $1.67 \times 10^{-3} \sim 2.83 \times 10^{-3}$/sec., which appear almost identical among different smples. For this process, the first order kinetics was assumed. In this case, Eq.(1) can be simply integrated as

$$c(t) = K[\exp(-kt) - \exp(-\kappa t)] \quad (4)$$

$$K = k\sigma_0/(\kappa - k) \quad (5)$$

where κ and σ_0 are the flow rate to volume ratio, (S/V), and the number of tritium initially adsorbed, respectively. The volume of the system, however, could not be determined explicitly because of the lack of exact knowledge on carrier gas flow in the present system. Therefore, κ is estimated through the analysis of the observed desorption curves as $\kappa = 6.67 \times 10^{-3}$/sec. As mentioned above, the rate constant, k, could be

determined from the decaying parts of thedesorption curves. With use of those values, the desorption curves could be reproduced. An example of the calculated desorption curves is shown in Fig. 6 along with the observed one which is the same desorption curve shown in Fig. 2 for the sake of comparison. It is seen that the calculated desorption curve agrees fairly well with the observations. The calculations using the same values of k and κ for other samples could also reproduce fairly well the respective observed desorption curves. This fact indicates that the species RD are identical irrespective to the different nature of the samples used. In addition, separate experiments showed that this species was condensable at liquid nitrogen temperature and dissoluble in water, strongly suggesting that it is HTO. In addition, it appears to be physically adsorbed HTO because it was readily ad/desorbed at room temperature and the ad/desorption behavior did not depend on sample nature.

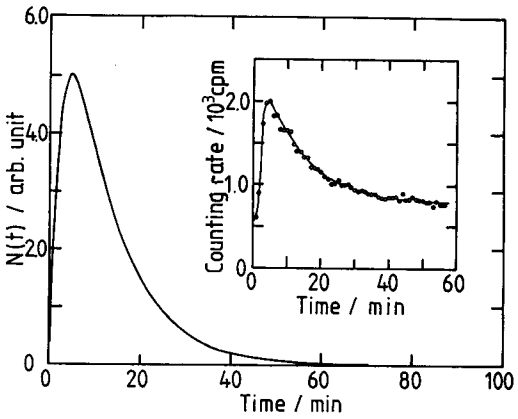


Fig. 6. An example of the desorption curves calculated through Eq.(4) : the in-set is the obsreved one for SS304 shown in Fig. 2.

There is an evidence that the tritium gas supplied from the getter is quite pure, containing no detectable H_2O[7]. The residual pressure of the vacuum system, however, is only 1×10^{-4} Pa, and the residual gas species are mostly H_2O and CO. Consequently, HTO is expected to be formed through the exchange reaction of HT and H_2O on the surfaces of stainless steel pipes used for constructing the vacuum system[8]. This appears to be responsible for the HTO adsorption on the sample surfaces during the room temperature exposure to the tritium gas.

3. 1. 1. 2. Surface residuum and high temperature desorption

Most of thermal desorption spectra showed predominant peaks in a temperature range of 450～480 K. In addition, it was seen that the amounts of HD were always about 10 times greater than those of SR. It should be noted that the escape depth of tritium β rays(E_{av}=5.7 keV) is several hundreds Angstrom for solid materials[9]. It means that the 2π measurements give the amounts of tritium being present in the surface layers within the above mentioned depth. On the other hand, the whole numbers of tritium ad/absorbed in the samples was measured with the thermal desorption spec-

troscopy under the present experimental conditions.

The (HD/SR) ratio has been considered to give the ratio between the number of tritium dissolved in the bulk and that adsorbed on the surface of a given material[10]. The present observations, however, appear not to be the case. This is because the desorption peaks were observed at almost equivalent temperature at about 460 K irrespective to different nature of the samples : namely, there was no characteristic feature of materials. In addition, the shapes of these peaks did not agree with those obtained from calculations assuming the diffusion controlled desorption process. The first order kinetics was also not the case.

Figure 7 shows an example of the calculated desorption spectra assuming the second order kinetics with $k_0 = 8.3 \times 10^{-9}$/molecules·sec and $\Delta E_r = 17.5$ kcal/mol. An observed desorption spectrum shown Fig. 3 is plotted together in this figure for comparison. It can be seen that both the desorption spectra agree fairly well with each other. It should be mentioned, however, that the values of k_0 and ΔE_r above are not necessarily unique ones beacuse other sets of them will also reproduce well the desorption spectrum. They can be determined explicitly only after systematic measurements of the desorption spectra. Nevertheless, the facts mentioned above strongly suggest that tritium adsorbed on the sample surfaces is responsible for the desorption peaks at about 460 K and desorbed through the second order surface reaction. Namely, this tritium species differs from that of RD.

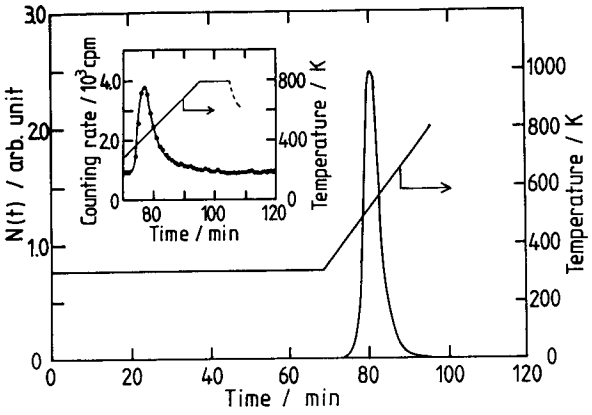


Fig. 7. An example of the desorption spectrum calculated through Eq. (1) and (2), accounting the linear temperature increase with time : the in-set is the observed one for A2219 shown in Fig. 3.

According to the above mentioned facts and discussion, the greater amounts of HD than those of SR appear not to be due to tritium dissolved into bulk. Although it is difficult at present to explain explicitly the reason of the large (HD/SR) ratios about 10, it is worthwhile to note that the roughness factors are usually in the order of 10 for the samples not specially prepared[11]. For those samples, a part of the β rays is expected to be shadowed and/or absorbed by salient parts of the sample surfaces, reducing the count rates of the 2π counter.

The separate experiments described above also revealed that the tritium species forming the 460 K peak was condensable at liquid nitrogen temperature. The species was, however, not soluble in water, being a clear contrast to the RD species. In addition, this peak disappeared or considerably reduced its intensity for the samples once heated up to about 700 K in the carrier gas folw or in vacuum. On account of the presence of contamination layers consisting of fat and/or hydrocarbons on the surfaces of as-received samples, the 460 K peak appears to be attributed to the fragments of this contamination layers[12], in which the adsorbed tritium is captured through hydrogen exchange reaction, hydrogenation reaction of double bond, and so on. It is also plausible to assume that isobutane contained in the carrier gas plays a role. Its detail, however, is an open question.

In the higher temperature side, there was a long tail or peaks as seen in Figs. 3 ~ 5. These higher temperature-side structures appear to depend on sample nature. At present, however, it is premature to discuss them because of the lack of systematic measurements.

3. 1. 2. Organic polymers

Hydrogen dissolves quite easily at room temperature in organic polymers as H_2 molecules[13]. This suggests that the 2π counter and desorption curves look at the same tritium species: in this case, it appears to be HT molecules dissolved in the FRP and epoxy resin[13]. Namely, a part of the molecules desorbed at room temperature and the other parts remained on/in the sample, which gave SR and HD. Therefore, the rate of desorption should be controlled by diffusion process and then the source term in Eq. (1) is described with Fick's law.

We assumed here a plane sheet with thickness, d, under boundary conditions as: 1) the tritium dissolved is initially distributed uniformly in the material, 2) the surface concentration is kept zero throughout the measurements. Namely,

$$C=0, \quad x=0, \quad x=d, \quad t=0$$
$$C=C_0, \quad 0 \leqq x \leqq d, \quad t>0$$

Then the rate of the desorption is described as[14]

$$N(t)=8(C_0D/d)\Sigma\exp[-\pi^2(2m+1)^2(D/d^2)t] \qquad (6)$$

where D is the diffusion constant having the temperature dependence as $D=\upsilon_d \exp(-\Delta E_d/RT)$ and m the integer.

The desorption curves and thermal desorption spectra could be calculated through substituting this equation into Eq.(1). Figure 8 shows an example of the calculations using $\upsilon_d = 8.3 \times 10^{-2}$ cm²/sec, $\Delta E_d = 7.5$ kcal/mol and d = 0.1 cm. The inset in the figure is the same desorption curve and spectrum shown in Fig. 5 . Although it should be kept in mind that the values of υ_d and ΔE_d have no physical significance owing to the similiar reasons as for Fig. 7 , it is clear that the shapes of the desorption curve and spectrum are quite similar to the observations. This indicates that the above mentioned mechanism plays a principal role for the ad/desorption of tritium by/from organic polymers observed in the present.

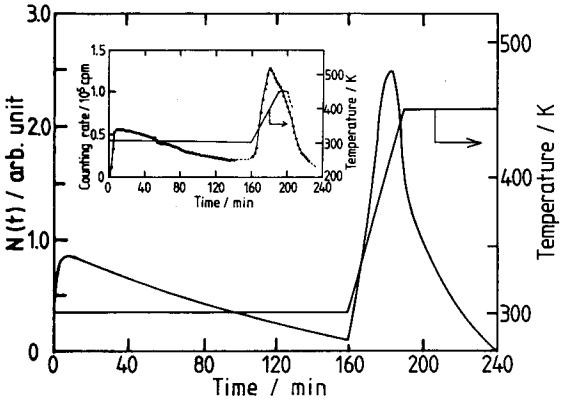
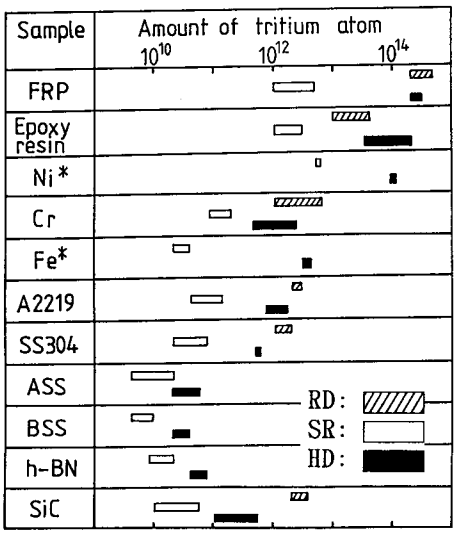


Fig. 8 . An example of the desorption spectrum calculated through Eq.(5) accounting the liner temperature increase with time: to be compared with those in Fig. 5 .

3 . 2 . Tritium ad/absorption activity and material characteristics

3 . 2 . 1 . Order of tritium ad/absorption

In Fig. 9 , the extents of ad/absorption are schematically drawn along with the observations for Ni and Fe which have been reported previously[10]. It should be mentioned that samples of Ni and Fe were mechanically polished to remove surface oxide and contamination layers before use. In the figure, it is seen that the order of ad/absorption was RD>HD>SR for each sample. Among different materials, the orders were as follows : 1) [Polymers, polished Ni]>[Cr, Fe, A2219, SS304, SiC]>[ASS, BSS, h-BN] for SR, 2) [Polymers]>[polished Ni]>[Fe, Cr, A2219]>[SS304, SiC]>[h-BN, BSS, ASS] for HD. With respect to RD, the order was [polymers]>[Cr, A2219, SS304, SiC]. This order appears similar to



* Cited from ref.10.

Fig. 9 . Comparison of the ad/absorption amounts among the samples.

that for RD, although there is a lack of data for some materials.

The points of interest in this figure were as follows: 1) Except organic polymers, the largest part of the ad/absorption was due to the RD species for each material. It was physically adsorbed HTO and it desorbed easily at room temperature. It amounted to about 1×10^{12} T/cm^2 (GSA) owing to the room temperature exposure for 1 hour at a HTO pressure of $1\times10^{-2}/60$ Pa : GSA denotes the geometric surface area. 2) The amounts of HD were about $10^{11}\sim10^{12}$ T/cm^2 (GSA) for conventional alloys such as SS304 and A2219. 3) For those alloys, the SR amounted to about 10^{11} T/cm^2 (GSA).

The first point mentioned above indicates that hazardous HTO vapor readily accumulates at room temperature on the inner walls of the tritium handling system even at a HTO partial presseure of 3×10^{-6} Pa. It will be released to environmental on opening the system to replace its components. In order to meet the requirement by ICRP, about 2.6 ℓ of fresh air per 10^{12} T/cm^2 (GSA) is necessary to dilute HTO to the level of 0.7 Bq/cm^3. Otherwise, the system should be rigorously purged with dry gases or evacuated to remove the adsorbed HTO before opening the system. With respect to the second and third points, it is also emphasized that the surface contaminant limit is 40 Bq/cm^2 for β-emitters, which is about 1/5 and 1/50 of the measured SR and HD, respectively, of SS304. They can be removed only by rigorous purging at higher temperature.

3. 2. 2. Material characteristics

3. 2. 2. 1. Organic polymers

The organic polymers used showed almost the same order of SR as that for Ni, whereas over 10 times greater than HD. These features should be due to relative ease of tritium diffusion and dissolution into these polymers as hydrogen molecules. Namely, conventional organic polymers have the diffusion constants about $10^{-7}\sim10^{-8}$ cm^2/sec and the solubility constants in the order of 1 when it is expressed as $C=KP$ where C and P are in the unit of [Pa•cc/cm^3] and [Pa], respectively, at room temperature[13]. Namely, the largest HD, SR and RD among those samples are attributed to the high solubility and diffusivity of hydrogen molecules in those materials at room temperature.

3. 2. 2. 2. Metals

As mentioned above, the RD species was physically adsorbed HTO. The species desorbed quite easily at room temperature and showed very similar desorption curves for all of the samples except organic polymers. Because the partial pressure of HTO

was considered to be kept almost equivalent for the sample exposures to the tritium gas under the present conditions, the relative amounts of RD should be valid as a measure of the roughness factors of sample surfaces. From this view points, it is interesting to note that the metallic samples show almost equivalent amounts of HD.

With respect to SR and HD, all of the metallic samples showed over two order of magnitude samller amounts than the respective values for Ni. In addition, the present samples did not have any features characteristic to sample nature, as seen for the peak around 460 K in the thermal desorption spectra. On account that the samples had been only washed with acetone and their surfaces had not been specially prepared to be clean before use, the relatively small values of SR and HD should be attributed to the non-clean surface of the as-received samples. Namely, the surfaces are expected to consist of respective oxides and, in addition, to be covered with contaminants such as fat. Both of them are known to act as poisons for adsorption as well as catalysis[3], resulting in the smaller amounts of SR and HD than cleaner surfaces. It should be mentioned here, however, the ad/desorption behavior is expected to change with the history of the system components such as heating cycles.

3. 2. 2. 3. Surface passivated metals and ceramic materials

The ASS and BSS samples showed the smallest amounts of SR and HD among the samples used. The ASS samples showed the SR and HD of about 1/10 of the respective values for SS304 and of 1/100 with respect to Ni. The surfaces prepared with the anodic oxidation, (ASS), are known to be covered with a surface layer of about 100 Å thickness consisting of Cr-oxide and Fe-oxide: there is the depletion of nickel in the surface oxide layers[15]. In addition, the ASS samples have mirror-like surfaces. According to the roughness factor measurements, the mirror-like surfaces usually have the roughness factors very near to unity[11]. This appears to hold for the present ASS samples. On the other hand, the metal surfaces of not specially prepared have the values around 10[11]. Consequently, it is expected that the shadowing effect of the β rays of ASS is considerably smaller than that of SS304. Taking those facts into account, it can be estimated that the anodic oxidation layer reduces the tritium adsorption about factor of 100 in comparison with as-received stainless steel and hence acts as a potential protection layer for tritium adsorption and permeation. The BSS samples were prepared with vacuum heating of SS304 doped with boron and nitrogen at 1100 K for 3 hours. After this pretreatment, the surface becomes to be covered with h-BN about 100 Å thickness[16]. Although there is a lack of knowledge on the roughness factor of this

sample, it is apparent that the h-BN layer can also reduce the tritium adsorption about factor of 10 or more and hence acts as a protection layer for the tritium adsorption and permeation.

The h-BN consists of planner layers with covalent bonds. The layers are stacked each other by van der Waals force. SiC exists in three differnt forms as diamond, zinc blend and wurtzite structures. In any of them, however, each silicon atom forms covalent bond with a carbon atom. This kind of compounds usually shows very small activity for hydrogen ad/absorption. This is also held for the present samples. With respect to a little larger values of SR and HD of these samples than those of BSS and/or ASS, it appears to be due to their porous nature.

4. Conclusions

In the present work, the ad/absorption of tritium on the non-cleaned surfaces of vacuum component materials were measured with use of tritium counting method and thermal desorption spectroscopy. The materials used were polymers (epoxy resin and fiber reinforced plastics), chromium, SS304 without/with passivation layers (ASS, BSS), aluminum alloy (A2219) and ceramics (h-BN, SiC).

Those samples were exposed at room temperature to HT gas equivalent to 67 Pa. The ad/absorbed tritium could be divided into three species: RD(being readily desorbed at room temperature), SR(surface residuum after the room temperature desorption) and HD(being desorbed at high temperatures). The RD species was the majority of the ad/absorbed tritium except the polymers and identified as physically adsorbed HTO. The SR and HD species appeared to be tritium atoms. Owing to sample heating, SR desorbed from the sample, forming thermal desorption spectra, in which a predominant peak was observed at about 460 K, irrespective to sample nature. In addition, the species forming the 460 K peak was condensable at liquid nitrogen temperature, but not dissoluble in water. The mechanism of this desorption is left as open question. The differences of the sample nature were only reflected as a tail or minor peakes at higher temperature side. With respect to the polymers, it was concluded that all of RD, SR and HD are due to the HT molecules dissolved in them.

The order of ad/absorption was roughly as [polymers]>[polished Ni]>[Cr, Fe, SS304, A2219, SiC]>[h-BN, ASS, BSS], which are quite different from that known for clean surfaces. This order appears to be partly due to the non-clean surface states and partly the roughness factors of the samples. In addition, the order of magnitude was about 1/100 in comparison with clean surface data. This is also attributed to the

non-cleaned surface states of the samples. Those results suggest that the tritium contamination/inventory/permeation would not be so much serious as the materials having clean surfaces. From the view point of safety and environmental aspect, however, the level of cotamination was still too high. This requires to establish the techniques preparing surface passivation layers over the component materials. With respect to this problem, anodic oxide layers and/or h-BN segregation ones are quite valuable for stainless steel. SiC coating is also expected to be valid for this purpose. It is, however, worthwhile to note that the ad/absorption activity of a material is expected to be sensitive to the history of the material such as heat cycles.

References

1) for example, R. S. Sokhi, K. S. Forcey, D. K. Ross and L. G. Earwaker, Nucl. Instr. Method. Phy. Res., **B40/41** (1989) 780.

2) J. S. Warton, C. E. Easterly, J. B. Cannon and J. B. Talbot, Fusion Technol., **12** (1987) 354.

3) G. C. Bond, "Catalysis by Metals", Academic Press, London and New York, (1962).

4) M. Matsuyama and K. Watanabe, Ann. Rept. Tritium Res. Centr., Toyama Univ., **7** (1987) 27.

5) H. Miyake, K. Ashida, M. Matsuyama, K. Watanabe and M. Sakurai, J. Vac. Soc. Japan, **34** (1991) 158 (in Japanese).

6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism (2nd Ed.)", John Wiley & Sons, New York (1961).

7) M. Matsuyama, H. Miyake, K. Ichimura, K. Ashida and K. Watanabe, Ann. Rept. Tritium Res. Centr., Toyama Univ., **6** (1986) 39 (in Japanese).

8) J. R. Robins, F. E. Bartoszek and K. B. Woodall, Fusion Technal., **8** (1985) 2455.

9) C. Feldman, Phys. Rev., **117** (1960) 455.

10) M. Matsuyama, Y. Araki, K. Ashida, H. Miyake, and K. Watanabe, Ann. Rept. Tritium Res. Centr., Toyama Univ., **8** (1988) 41 (in Japanese).

11) for example, H. Kumagai, G. Tominaga, Y. Tuzi and G. Horikoshi, "Vacuum Science and Engineering (in Japanese)", Shokabo, Tokyo (1970) : K. Watanabe, S. Maeda, T. Yamashina and A. G. Mathewson, J. Nucl. Mater., **93/94** (1980) 679.

12) for example, N. Inoue, K. Ichimura, K. Watanabe and T. Takeuchi , Ann. Rept.

Tritium Res. Centr., Toyama Univ., **3** (1983) 33.

13) H. Miyake, M. Matsuyama, K. Ashida and K. Watanabe, J. Vac. Sci. Technol., **A1** (1983) 1447.

14) H. S. Carslaw and J. C. Jeager, Conduction of Heats in Solids (2nd Ed)", p.96, Clarendon Press, Oxford (1959) : p.179 in Ref. 11

15) T. V. Rao, R. W. Vook, W. Meyer and A. Joshi, J. Vac. Sci. Technol., **A4** (1986) 1604 : K. Ashida et al., not published.

16) D. Fujita and T. Homma, J. Vac. Sci. Technol., **A6** (1988) 230.