Interactions of Hydrogen Isotopes with Metals and Alloys

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Tritium decontamination is one of the important problems for the safety of D-T fusion reactors. The experimental results showed that UV light combined with IR irradiation was effective in decontaminating tritium from metals and alloys. The desorption rate of 96% was achieved at 150℃. Desorption at the temperatures of 75℃ to 150℃ was enhanced further by replacing argon with dry air. The behavior of tritium sorption, thermal desorption and photo-desorption was investigated for varying metal surfaces.

1. Introduction

Tritium decontamination is one of the important problems for the safety of D-T fusion reactors. Hirabayashi et al applied a wet chemical approach using dilute HCL and $CuSO_4$-H_2SO_4 solution to decontaminate tritium from 316 stainless steel [1-7]. In the present work, a dry technique using simultaneous UV (ultraviolet) and IR (infrared) irradiation was proposed for the tritium decontamination of metal surfaces.

2. Experimental Procedure and Results

2.1 Sample preparation

The rectangular SUS sample was cut into 30x10x1.25mm, and made from a cold-rolled sheet of new austenitic type 316 stainless steel. It is composed of Cr, 17.41%; Ni, 12.12%; Mo, 2.09%; Mn, 1.27%; Si, 0.66%; P, 0.033%; C, 0.016% and balanced by Fe. The SUS sample surface was ground in water with sand paper down to No.1200 and polished with 5 μm and 0.05 μm of alumina suspention liquid sucessively. After polishing, it was washed with distilled water and then with acetone, to wash it in acetone by an ultrasonic cleaner. In order to suspend by the end of the thermal couple in the irradiation chamber, a hole was drilled at one end before polishing. After weighting, the surface area was measured to make a non-electrical plating with Cu, Ni and Au on stainless steel surface. Other samples used were Au, Cr, CrO-SUS and Ti.

2.2. Tritium sorption and thermal desorption

The tritium sorption was carried out in a glass vessel which was connected to a 10^{-6} torr glass high vacuum system. After baking out at 300℃ in the vacuum for 2 hrs, the sample was exposed to HT-gas (the ratio of H/T: 52.16) of 100 torr at 20℃ for 7 days, and then removed and evacuated at room temperature for 20 minutes (the tritium concentration was 40.32 TBq/mol). After evacuation, the still remaining tritium was defined as chemical sorption tritium. To break the vessel, take out the sample and put it in the the thermal desorption system. The TPD temperature was raised at a rate of 5 C/min from 20℃ to 1000℃. Then the sample was kept at 1000 ℃ for 20 minutes. The tritium was desorbed in the form of HTO or HT, which was carried out successively from the infrared image furnace to a liquid scintillation and a gas proportional counter by He carrier gas. In order to prevent any contamination of the wall, at the outlet of the furnace, H_2 gas was damped with water.

The ratio of tritium activity between the different surfaces is listed in Table 1

In Table 1, Column 1 is the ratio of water and gas in one sample, and Column 2, 3, and 4 are the ratios between SUS and other materials, in which SUS equals 1.00.

Table 1 The ratio value of HTO and HT between samples

	HTO/HT	HTO	HT	HTO+HT
SUS	2.30/1	1.00	1.00	1.00
Cu-SUS	4.11/1	0.97	0.54	0.83
Ni-SUS	1.37/1	0.85	1.42	1.02
Au-Ni-SUS	11.00/1	0.65	0.14	0.50
Au-Cu-SUS	13.30/1	0.35	0.06	0.26
Au	4.83/1	0.25	0.12	0.21
Cr	4.74/1	0.31	0.15	0.26
CrO-SUS	14.60/1	0.17	0.03	0.13
Ti	0.01/1	0.32	89.60	27.40

From Table 1, the order of HTO or HT sorption are as follows:

HTO/HT: CrO-SUS, Au-Cu-SUS, Au-Ni-SUS > Cu-SUS, Cr, Au > SUS > Ni-SUS > Ti

HTO: SUS > Ni-SUS, Cu-SUS > Au-Ni-SUS > Au-Cu-SUS, Cr, Ti > Au > CrO-SUS

HT: Ti >> Ni-SUS > SUS > Cu-SUS > Au-Ni-SUS, Au, Cr > Au-Cu-SUS > CrO-SUS

HTO+HT: Ti >> SUS, Ni-SUS > Cu > Au-Ni-SUS > Au-Cu-SUS, Cr > Au > CrO-SUS

From this experiment one can conclude that:

1) All of surfaces have a single HTO peak at around 300℃;

2) HT has 3 peaks of HT-1, HT-2 and HT-3 for SUS and other materials;

3) HTO has a major sorption peak for Au and CrO-SUS. At room temperature, Ti sorbed HT at two orders higher than SUS;

4) The inert metal Au surface also sorbs tritium at room temperature.

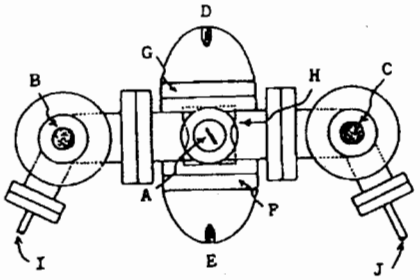
2.3 Tritium sorption and Photo-desorption

The procedure for tritium sorption is the same as in section 2.2. The apparatus for UV plus IR stimulated desorption is shown in Fig. 1 which consists of an irradiation chamber in the center, two IR lamps at the front and back of the chamber, and two 3.9 W low pressure Hg UV lamps were at the right and lift sides of the chamber. The UV-lamp was enclosed in the system by a standard stainless steel fringe, but the IR-lamp was outside the system and there were two silica windows installed at both sides of the chamber to allow the IR light to focus on the sample. The sample position was fixed at the end of the thermal couple by a hole which was drilled at the top of the sample. The position of the sample in the chamber was adjusted to a 45 degree angle opposite to each of the four surrounding lamps. The flow gas was introduced from the inlet at the bottom of each UV-lamp, to control the gas flow rate in the range of 100 to 120 cc/min. The outlet for flow gas was installed under the chamber. There were one control valve for the outlet, and one for each of the inlets, these were used to open and close the chamber. The desorption temperature was controlled by a thermal couple and an IR-lamp controller system. Usually, the temperature raising time was one minute, and the duration of the irradiation holding time was 180 minutes.

In order to depress the tritium contamination on the tube wall, the hydrogen gas (wet with water) was introduced next to the outlet. After the flow gas had passed through the chamber, the desorbed tritium was mixed in it and then passed through a water bubbler to absorb the HTO and then to a Cu_2O furnace to oxidize HT to HTO. Silica and P_2O_5 dryers were placed between the water bubbler and the furnace to remove any water vapor in the flow gas. The HTO part, which was transformed from HT, was also absorbed by the second water bubbler. The duration for absorption of HTO in one water bubbler is 15 minutes. After each of 15 minutes, to change one water bubbler to another by using a T-type controlling glass valve and to take 1 ml liquid from the 10 ml HTO absorption water solution in the bubbler. The 1 ml liquid, which contained HTO, was mixed with 10 ml of liquid scintillation solution (Aquasol-2, Biotechnology System NEN research products Du Pout). The radioactivity of tritium was measured by an on-line program of PACKARD TRI-CARB 300 liquid scintillation system (PACKARD INSTRUMENT CO INC).

The UV radiation effect on speeding up the desorption of tritium was observed by a two-step experimental procedure. First, it was irradiated by IR at 150℃ from 0 to 90 minutes; then, by UV plus IR at the same temperature from 90 to 180 minutes. The results of SUS, and the cold-rolled Au sheet (before or after annealing) are shown in Figs. 2 and 3.

A photo-desorption experiment was made to determine the tritium desorption per cent (PD %) with UV plus IR within the whole process heated at 75℃, 150℃ and 300℃. The results are shown in Fig. 4.



A: Sample, B and C: UV lamp, D and E: IR lamp, F and G: Quartz window, H: Hexahedral fitting I and J: Inlet for dry air flow

Fig. 1 Schematic diagram of the apparatus for photo-stimulated desorption of tritium from the surface of metals and alloys

Another type of photo-desorption experiment was performed by dry air replacing the argon as the flow gas, as oxygen can be excited by 184 plus 254 nm UV light and turned to active oxygen and ozone, which might be more chemical active in oxidizing the surface materials to remove tritium out. The experiment procedure was the same as for argon gas, only no wet hydrogen has added to the outlet. Fig. 5 is the two-step mode results.

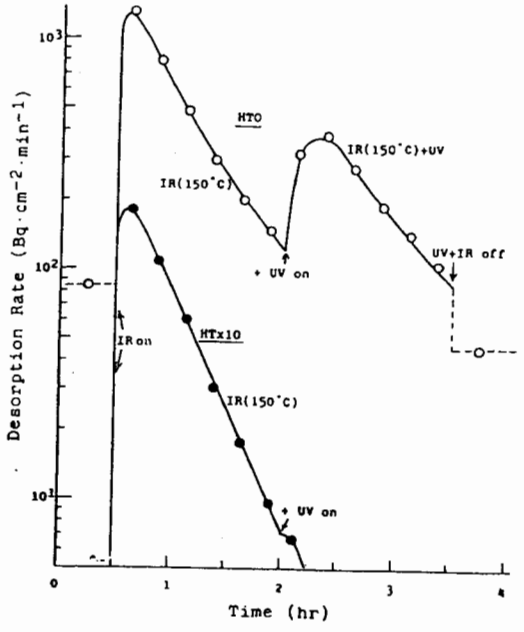


Fig. 2 Desorption rate of tritium from SUS under two-step photo-desorption mode at 150℃

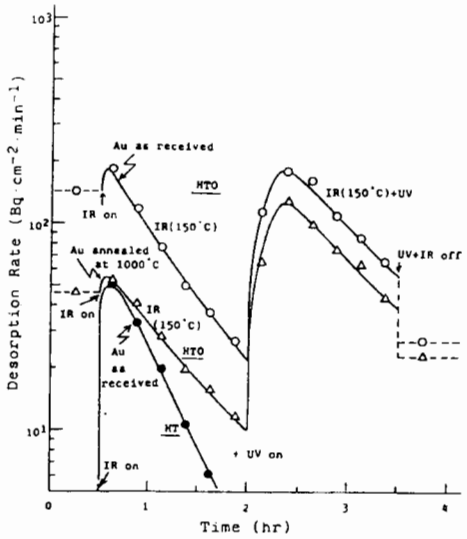


Fig. 3 Desorption rate of tritium from a gold sheet before and after annealling under a two-step photo-desorption at 150℃

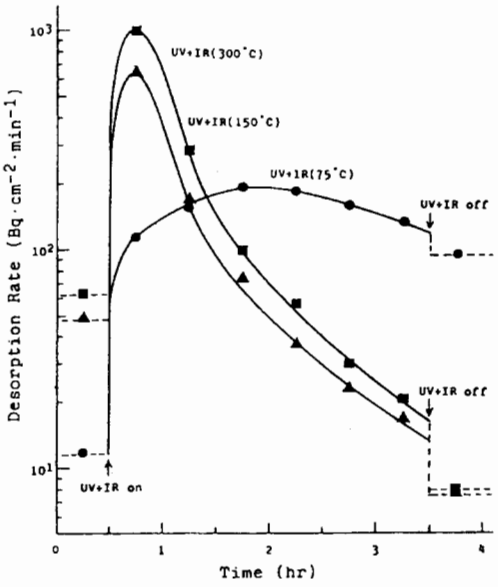


Fig. 4 The comparison of tritium desorption rate from SUS under UV plus IR mode at 75℃, 150℃ and 300℃

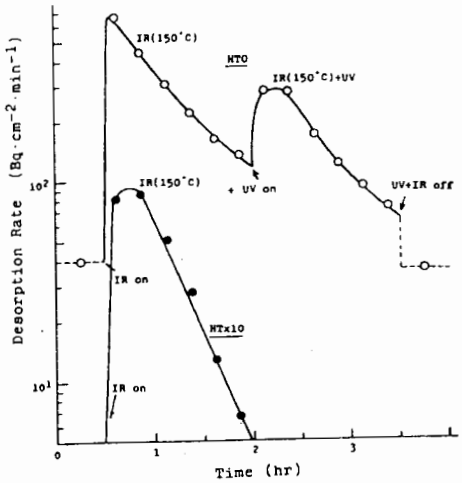


Fig. 5 Desorption rate of tritium from SUS under two-step mode and dry air atmosphere at 150℃

Table 2, PD % of photo-desorption of SUS

Sample No	Irradiation* Conditions	Total HTO+HT (Bq/cm^2)	Residual HTO (Bq/cm^2)	HT	HTO /HT	PD %
PT-13	IR 300C	31801	193	26	7.42	99.31%
PT-11	IR+UV 300C	52109	81	259	0.31	99.35%
PT-14	IR 150C	43239	2697	218	12.4	93.25%
PT-12	IR+UV 150C	36232	1292	121	10.8	96.10%
PT-27	IR,IR+UV150DA	54717	2228	1251	1.78	93.64%
PT-16	IR, IR+UV150	91369	6152	2087	2.95	90.18%
PT-17	UV, IR+UV150	56573	5711	2148	2.66	86.11%
PT-24	IR 75C	66227	25018	3401	7.36	57.09%
PT-23	IR+UV 75C	57941	23890	1366	17.5	56.41%
PT-18	IR, IR+UV75	61249	18344	3834	4.78	63.79%
PT-26	IR,IR+UV75DA	65685	21367	759	28.2	66.31%
PT-28	UV,IR+UV75DA	70180	17553	1268	13.8	73.18%
PT-10	UV 35C	79408	47177	11357	4.15	26.29%
PT-25	UV 35 DA	37291	22845	710	32.2	36.83%

* DA means in dry air atomsphere. Elsewhere argon was used

2.4 Photo-desorption per cent under different experimental conditions

The photo-desorption per cent (PD %) of SUS is listed in Table 2, other surfaces are listed in Table 3.

Table 3, to decontaminate tritium from different surfaces (at 150℃, by IR for 90 min, then by UV plus IR for 90 min)

No	Materials	Total HTO+HT	Residual HTO	HT	HTO/ HT	PD %
PT-16	SUS	91369	6152	2087	2.948	90.18%
PT-22	Ni-SUS	145658	2329	9531	0.244	91.85%
PT-21	Cu-SUS	96366	21051	3590	5.864	74.43%
PT-19	Au-Cu-SUS	94352	19448	14327	1.357	64.20%
PT-15	Au sheet	42078	10137	693	14.63	74.26%
PT-20	Au sheet annealed at 1000 C	21081	2980	914	3.260	81.53%

Table 4 The relationship between STM surface roughness with PD %

	Roughness (STM Z※SD.)	PD %
Au sheet	0.0152	74.26%
polished-SUS	0.0378	90.18%
annealed-Au	0.2023	81.53%
Ni-SUS	0.2420	91.85%
Cu-SUS	0.3056	74.43%
Au-Cu-SUS	0.4816	64.20%

From the above there tables, one can see that for SUS:

1) At 300℃, the major effect for tritium desorption is IR irradiation, but UV can speed up the desorption rate and UV is more effective in removing HTO;

2) At 150 ℃ , the optimal condition is UV combined with IR. Either way, dry air flow is more effective than argon for tritium desorption and especially for removing HT;

3) At 75 ℃ , UV irradiation is more effective under dry air gas flow (PT-28);

4) Even with UV only, dry air is better than argon (PT-25);

5) To compare with SUS , the coated SUS and gold sheet are less effective in removing tritium. The order of difficulty is related to the STM surface roughness as can be seen in Table 4.

The light, especially for UV, might be shaded by uneven surface which causes difficulties in tritium desorption.

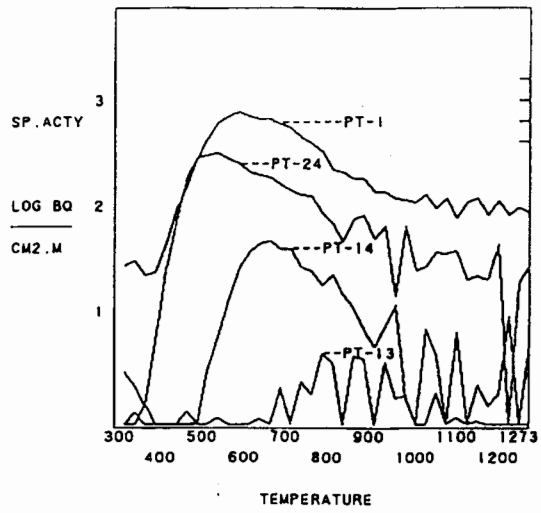


Fig. 6 A comparison between the TPD spectrum of residual HTO on SUS after photo-desorption and the original TPD spectrum of sorbed HTO on SUS (PT-1). PT-24, PT-14 and PT-13 are the TPD spectrum of residual HTO on SUS after IR irradiation at 75℃, 150℃ and 300℃ respectively.

2.5 TPD spectrum

All of the TPD spectrum of residual tritium coupled with the original TPD spectrum of sorbed tritium (PT-1) on SUS surfaces are shown in Fig. 6 to 7.

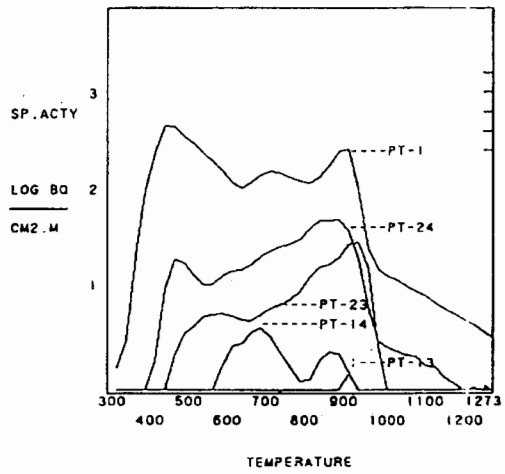


Fig. 7 A comparison between the TPD spectrum of residual HT on SUS after photo-desorption and the original TPD spectrum of sorbed HT on SUS (PT-1). PT-24, PT-14 and PT-13 are the TPD spectrum of residual HT on SUS after IR irradiation at 75℃, 150℃ and 300℃ respectively. PT-23 is the TPD spectrum of residual HT on SUS after IR plus UV irradiation at 75℃.

From Fig. 6 and Fig. 7, the following observations can be made:

1) As soon as the residual tritium becomes lower, the peak will move to a higher temperature.

2) Some HT peak will disappear when the tritium levels are lower. The order of residual HT peak to be lost is HT-1, HT-2 and then HT-3. The HT-3 peak is more difficult to remove under the present experimental conditions.

3. Conclution

From the present work, the following points could be concluded:

1) 254 plus 184 nm UV light combined with IR irradition was effective in decontaminating tritium from a metal surface. At 150 ℃ and 300 ℃, the desorption per cents were 96 % and 99 %, respectively. Dry and low temperature conditions are recommended for tritium decontamination.

2) The UV effect on the stimulation of tritium desorption was proved by a two-step experimental procedure. there was about a one order increase in the tritium desorption rate after a 3.9 W Hg UV-lamp was switched on.

3) Nearly all of the tritium was measured in HTO form. Photo-oxidation occurred during desorption.

4) To replace argon with dry air as flow gas, caused a positive effect on desorption from 75℃ to 150 ℃.

5) After photo-desorption, the residual tritium TPD peaks moved to a higher temperature.

6) A relationship between desorption per cent and surface roughness was confirmed by the STM image measurement (refer to the Table 4). UV light may be shaded by uneven surfaces which causes difficulties in tritium desorption.

7) The behavior of sorption, thermal desorption and photo-desorption on different metal surfaces was observed. It is certain that tritium could be sorbed on gold, particularly on a coated gold surface (mainly in the HTO form). It is more difficult to remove tritium from a gold surface. After annealing at 1000 ℃, the tritium sorption amount on gold can decrease by half and desorption is higher than before annealing. Titanium sorbed tritium about two orders higher than stainless steel.

8) The TPD spectrum shape of HTO on different surfaces was similar to SUS and HT had three peaks also.

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