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Update on observation of low energy emissions from deuterated arid hydrated palladium

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Low energy radiations were observed to be emitted from deuterated and hydrated palladium samples. The radiations were not observed when the samples were kept in vacuum or in an atmosphere of nitrogen, helium or argon. However, radiographs of reduced intensity were observed when the samples were kept in pure oxygen or hydrogen. Using a sensitive densitometer, it was observed that a small fraction of the radiation is transmitted through a 2 μm thick aluminised polycarbonate filter.

In our previous paper [1] we have reported that palladium (Pd) or its alloys with silver (Ag), when loaded with deuterium (D_2) or hydrogen (H_2), emit copious low energy radiations. This phenomenon is completely reproducible and its occurrence has been confirmed by others [2,3]. The energy of these radiations appears to be between a few tens and a few hundreds of eV and most likely these radiations consist of electrons. We report here our further investigations.

Loading of Samples

To standardize the results only gas loading method was utilized. In this technique the sample was first heated to 600°C in a vacuum chamber ($< 10^{-5}$ mbar) for two hours and then allowed to cool in an atmosphere of H_2 at 1 bar. The atomic loading ratio was estimated from the drop in pressure. In the new studies pure Pd metal samples of 18 mm in diameter and 2 mm thick (obtained from Hindustan Platinum Ltd, Bombay, India) were loaded. Ten freshly. loaded and six reloaded samples were used for this test. Only H_2 loaded samples were used except where fusion products such as heavy charged particles were to be investigated, as it was felt that D_2 loaded samples may emit interfering radiations such as electrons and X-rays from anomalously generated tritium in the deuterated Pd. Only analytical reagent grade hydrogen having ≤ 4 ppm of oxygen and ≤ 100 ppm of nitrogen was used for loading. The D_2 gas used for loading had tritium content $\simeq 10^{-4}$ Bq/mL.

Autoradiography Techniques

For all autoradiography measurements Indu brand 'Polyester X-ray Film' (from Hindustan Photo Films Ltd) was used. The film had X-ray sensitive coating of medium grain size (10 to 15 μm diameter) on both the sides. The film was experimentally found to be sensitive to white light, X-rays, electrons and heavy charged particles. The film was insensitive to red light and longer wavelength radiations. The film was developed using Superol brand of developer and fixer (from May and Baker Co. of India) following a standard procedure.

The fogging density referred to hereafter as density, is defined as (–)Log (Transmitted light/ Incident light) for white light and was measured using a densitometer. The instrument was calibrated using neutral density filters and was found to have a threshold for density measurement of $\simeq 3 \times 10^{-3}$ Log units.

Autoradiography in Various Gases

In all the autoradiographs obtained (under any condition), the fogging was always observed only on the side of the film facing the samples, in spite of the fact that the X-ray film is transparent to optical radiation and had sensitive coating on both sides. This confirms the low range of the radiations and absence of optical emissions.

Vacuum – No fogging above threshold could be observed on the autoradiographs when the PdH_x samples were kept in vacuum ($< 10^{-2}$ mbar). The photographic films were typically kept 0.2 mm away from the samples for 96 h. In the case of the samples kept as control in air, an average density of 0.08 was observed on the autoradiographs. The samples kept in air and vacuum were then interchanged. After 96 h of exposure again no fogging, above threshold, was observed on the autoradiographs obtained from the sample kept in vacuum, while with the sample kept in air, an average density of 0.06 was observed.

Nitrogen, helium and argon atmosphere – Some samples were also kept in atmospheres of nitrogen, helium and argon gases. The gas pressure was retained slightly ($\simeq$ 50 mbar) above one atmosphere. The exposure time in all the cases was 96 h. No fogging, above threshold, was observed on. any of these autoradiographs, whereas an average density of 0.06 was observed on the autoradiographs of control samples kept in air as earlier.

Hydrogen atmosphere – Some samples were also autoradiographed in an atmosphere of hydrogen. The gas pressure was again kept slightly ($\simeq$ 50 mbar) above one atmosphere. The gas was of analytical reagent grade. After 96 h of exposure, the fogging obtained on the autoradiographs was just discernible over threshold (see Table 1).

Oxygen atmosphere – PdH_x samples kept in oxygen atmosphere at pressure of $\simeq$ 50 mbar above atmosphere; for 96 h, fogged the autoradiographs to an average density which was 40 to 60% less than what was obtained with control samples in air (see Table 1).

Autoradiography with Filters

By means of a sensitive densitometer, it was possible to measure density of even very faint autoradiographs. Fogging could thus be detected when thin filters were kept between the film and loaded samples. The filters used were 2 μm aluminised polycarbonate foil (14% aluminium, 0.25 mg/cm^2) in one or several layers. Weak fogging was always measured with one layer of such a filter (see Table 1). With two layers of filters fogging was observed only in one instance (barely above threshold). No fogging was ever observed, above threshold, with three or more layers of filters.

Table 1 - Density of autoradiographs under various conditions

Density averaged and normalised to 24 h exposure time

	Condition for autoradiography	Density × 10^{-3}
1	In normal air atmosphere	80
2	In oxygen atmosphere	32
3	In hydrogen atmosphere	3.5
4	In air with 0.25 mg/cm^2 filter	6.0
5	In air with + 0.67 kV/cm field	230
6	ln air with - 0.67 kV/cm field	210

Long duration (exposure time 400 h) autoradiographs were obtained using three PdH_x samples covered with no, one and two filters (2 μm thick aluminised polycarbonate) respectively. The autoradiograph obtained with one filter had $\simeq$ 25% of its area fogged to a density of 0.25. The autoradiograph with two filter foils had no fogging above threshold, while the one without filter was uniformly fogged to a density of 0.36.

Photomultiplier Tube and Photo Diode Studies

The loaded samples were placed (in air) on a low noise photomultiplier tube (Philips XP 2041), having 2.1 eV to 5.5 eV (10% to 90%) spectral range with the sensitivity peaking at $\simeq$ 3.1 eV. Threshold light detection of the tube was 10^{-14} W (2×10^4 photons/s). No light emission could be measured. For near infrared measurement the samples were kept on a photo diode (EG & G SGD 100), having 1.1 eV to 3.5 eV (10% to 90%) spectral range, peaking around 1.3 eV. Threshold of light detection was 10^{-7} W (5×10^{11} photons/s). No radiation could be observed using photo diode also.

Attempts were also made to observe any signal from the photomultiplier tube when one of the following ‘high energy radiation to light converters’ was placed between sample and PM tube: (1) 3 mm plastic scintillator (NE 102A), (2) Zinc sulphide screen, (3) Rare earth screen

normally used to enhance the sensitivity of medical X-ray film. In none of the cases any signal above threshold was observed when PdH_x sample was kept in contact with the converter in air.

Windowless Gas Flow Detector Measurements

One hydrogen loaded palladium sample was kept for counting in a 2 π geometry windowless gas flow proportional detector, operated with commercially available liquid petroleum gas (cooking gas) as counting medium. The sample was kept in the detector for one month and every day measurement was made for ≃ 3 h. The average counts observed with and without the sample were 4.0×10^{-2} counts/s and 3.7×10^{-2} counts/s respectively. The difference is not statistically significant (< 2 σ).

Charged Particle Measurements

Recently experiments have been conducted in which heavy charged particle emission was searched from deuterated Pd as well as its alloy with silver by solid state nuclear track detectors (CR-39). The sample was kept over the film for few tens of hours and then it was processed and tracks counted by optical means. Our preliminary studies (see Table 2) indicate that emission from pure deuterated Pd samples was, at best, sporadic [1]. However emission from silver palladium alloy (Ag 25% Pd 75%, procured from Johnson Mathey, USA) thin foils (50 μm) have shown > 70% reproducibility (≃ 10^{-4} - 10^{-3} particles/s). As can be seen from Table 2 that the charged particle emission is significantly enhanced when D^2 was loaded in sample as compared to virgin and H_2 loaded samples. The charged particle emission was varied from 10^{-4} to 10^{-3} particles per second. The details of the charged particle emission studies will be presented in a separate paper under preparation.

Results and Discussions

Experimental findings – Autoradiographs have been observed in oxygen and air atmospheres but not in helium, argon and nitrogen atmospheres. This confirms the following conclusions drawn earlier [1] namely that fogging is not due to (i) pressure effects (ii) some chemical reaction between sample and film nor (iii) tritium or any other radioactive contaminant. The photo multiplier measurement confirms that optical radiations, if any, produced by recombination of oxygen with hydrogen, are so weak in intensity that fogging cannot be attributed to these.

Table 2 - Charged particle emission measurements (CR-39)

Sample number	Exposure time h	Net tracks ± 2σ		
		Side A	Side B	Side A + Side B (particles/s*)
Deuterium loaded				
1	65	24 ± 29	37 ± 32	61 ± 43
2	65	40 ± 38	109 ± 40	149 ± 56
3	65	55 ± 31	66 ± 36	121 ± 48
4	72	26 ± 39	19 ± 28	45 ± 49
5	72	30 ± 29	8 ± 31	38 ± 42
6	72	31 ± 28	29 ± 27	60 ± 40
7	72	29 ± 26	29 ± 27	60 ± 40
Total	966			555 ± 121
				$(7.3 \pm 1.6 \times 10^{-4}/s)$
Control samples				
(A) Hydrogen loaded				
1	116	32 ± 37	14 ± 38	46 ± 54
2	116	4 ± 33	17 ± 34	21 ± 48
Total	464			67 ± 72
				$(1.8 \pm 2 \times 10^{-4}/s)$
(B) Virgin				
1	116	49 ± 39	20 ± 38	69 ± 54
2	116	-21 ± 24	30 ± 41	9 ± 54
Total	464			78 ± 77
				$(2.1 \pm 2.1 \times 10^{-4}/s)$
Total of control samples				
	928			145 ± 105
				$(2.0 \pm 1.4 \times 10^{-4}/s)$

* Efficiency 22%

Since no fogging, above detection threshold, was observed in vacuum, most of the usual techniques, such as mass spectrometry, etc., cannot be used to study the low energy radiations. The only way to estimate the energy of the emitted radiations is to observe the transmission through thin filters. The transmission through 2 μm aluminised polycarbonate (lie threshold 1 keV} was such that the autoradiograph (for 96 h exposure} was just barely observable. Therefore, no accurate measurement could be made. However, the rough estimate of attenuation of intensity through this filter (assuming that the radiation is monochromatic) suggests that its energy (normally) is in the range of 300-400 eV. These low energy radiations cannot excite solid scintillators or converters as all these have a few μm thick protective layer [4] and the radiations are unable to cross it.

So far, only in one long duration exposure (400 h), with one filter, has a very intense fogging (as compared to 96 h exposure} been observed. In this case $\simeq$ 25% of the area (in random spots) of the autoradiograph was fogged to a density which was 0.7 of the sample without filter. This suggests sporadic emission of radiations of several keV energy from PdH_x samples (similar emissions were also sporadically observed from TiH_x and TiD_x samples [1]).

The presence of oxygen or air appears to be necessary to observe strong radiographs. It is likely that oxygen is assisting the phenomenon. (Some other impurity present in oxygen as well as in air causing this phenomena although unlikely, cannot be ruled out). However, there appears to be an optimum concentration (< 100%) of oxygen in atmosphere at which the fogging is maximum. The fogging in oxygen and air should be equal, if not higher, if the fogging were due to direct recombination of oxygen and hydrogen (chemiluminiscence). However, it is possible that the recombination is triggering some phenomenon which results in emission of high energy radiations. If recombination is taking place it should emit radiations in infrared (1.48 eV is produced per 1/2 H_2O produced, the equivalent electromagnetic radiation is in infrared region) and visible region. If the reaction of hydrogen with oxygen is responsible for these radiations then the absence of these infrared radiations is puzzling.

A small degree of fogging was also obtained when autoradiography was done in hydrogen. This could not be because of trace impurity of oxygen in hydrogen, as no fogging was observed with nitrogen, even though it had higher oxygen impurity. This aspect also requires further investigations.

No counts were observed when the sample was kept inside a gas (methane) flow proportional detector (in reference 1 it was kept outside in air), this could be due to the absence of oxygen in the gas in the gas flow detector. Attempts are underway to operate such a detector with air or oxygen. Initial attempts have not succeeded as oxygen is an electronegative gas.

Charged particle measurements show that 70% of the deuterium loaded samples have low intensity ($\simeq 10^{-4}$ particles/s) emission. In case of control sample, the much lower charged particle emission observed, is perhaps due to natural radioactivity.

Possible mechanisms – High energy emissions from dielectrics and metals coated with their oxides are not unusual. These emissions could be due to lattice cracking [5] or triboluminescence [6]. The low energy emissions observed from PdH_x may be due to sudden

rupturing of oxide layer on Pd by hydrogen stored in it. For sustained emission of these radiations ruptured oxide layer should be reformed, and for this oxygen or air atmosphere is required. However, in other materials where lattice cracking or triboluminescence has been observed most of the radiations are reported to be in optical or lower energy range and only a small fraction bas higher energy. Since we have observed no detectable radiation around optical range, it is likely that lattice cracking or triboluminescence may not be responsible for these emissions. However, there are several other phenomena in condensed matter which suggest that short lived large energy fluctuations do take place [7]. These fluctuations can impart 100 to 1000 times the average energy.

The energy released in $H_2 - O_2$ recombination reaction is 1.5 eV, if a few hundred to thousand times this energy gets transferred to a D ion then normal hot fusion can take place resulting in emission of neutrons and energetic heavy charged particles ($\leq 10^{-2}$/s), if there is a pathway to transfer the chemical recombination energy to deuterons. This may be possible only for certain metallurgical compositions and conditions.

The charged particle and neutron bursts from PdD_x system may be more likely if it is kept in air/oxygen. Since the perturbation to the lattice due to $H_2 - O_2$ recombination is much higher than by electrolysis or by thermal cycling. Our charged particle measurements seem to support this.

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