POSITRON LIFETIME STUDIES ON SYSTEMS OF PALLADIUM FILLED GALVANOSTATICALLY WITH HYDROGEN OR DEUTERIUM

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ABSTRACT

The positron lifetime spectroscopy was used to investigate the electron structures of crystal lattice and its defects in palladium samples filled galvanostatically with hydrogen and deuterium, respectively. The results have indicated that the positron lifetime were all the same between hydrogen and deuterium filled samples in which the positron lifetime τ_1 increased about 10%, corresponding to the volume expansibility after the formation of hydrides PdH or PdD phases during electrolyzing commom water or heavy water with Pd cathode; and will not change with time in 3 weeks after stopping electrolysis; but could be recovered to 116±1 ps, the value in polycrystalline pure palladium, after annealing at high temperature.

Keywords: Positron lifetime Hydrogen Deuterium Palladium

I. INTRODUCTION

There are several common considered mechanisms for " cold nuclear fusion" [1], among which the so- called " piezonuclear- fusion" resulting from the tightly compressed deuterium in palladium lattice, and "micro hot- nuclear fusion" caused by strong electric field in the micro cracks of palladium, during the off- equillibrium process of electrolysing, and so on, relate to the electron structures of palladium lattice and its defects.

Positron- annihilation spectroscopy (PAS) is an effective and sensitive means for studying electron structures of the crystal lattice, especially, the defect in condensed matter[2]. Therefore, PAS is also a very useful tool for the investigation of the Pd- H and Pd- D systems.

In the present work, the positron lifetime spectroscopy (PLS) had been used to study the similarity of electron structures for Pd- H and Pd- D systems and behaviors of hydrogen and deuterium, which were compressed galvanostatically into sheet samples of palladium from H_2O and D_2O, respectively.

II. EXPERIMENTAL

1) Experimental processes Smelting and rolling of 2 mm thick sheets of 99.99wt% Pd—Cutting into 8 squares of 15mm×15mm as 4 pairs of samples (No.1—4)—Cleaning and drying—Annealing(550°C,8h)—Measuring of PLS—Electrolyzing common water

with the samples 1 and 3 as cathodes, and heavy water with the samples 2 and 4 as cathodes—Measuring of PLS after different time—High temperature annealing (>1100 °C,8h,cooling slowly with furnace)—Measuring of PLS—Data analysing.

2) Electrolysis conditions Using Pt foil as anode, Pd samples as cathode, 5.5– 7.8 volts of DC potential differences across each cell at a constant current of 800 mA, H^+ and D^+ had been compressing galvanostatically into Pd samples from 0.5 mol/l LiOH in H_2O and LiOD in D_2O solutions for 5 h respectively.

3) Measurement of PLS Using the positron lifetime spectrometer of Ortec fast– fast coincidence system and BaF_2 detectors, with a resolution function of FWHM = 230 ps, at the room temperature 20± 1°C, each pair of samples was measured repeatedly with 10^6 counts for each spectrum after the measurement system stabilizing sufficiently for two weeks.

4) Data analyses Using the program of Positronfit– Extended[3] modified for PC computers, WUPCPE[4], each PLS was analysed by a weighted least- squares fitting to a model: a sum of three exponentials convoluted with a resolution function which is a sum of two gaussians ($FWHM_1$= 231ps, $Intensity_1$ = 97.7%, $Shift_1$ = 0.00ps; $FWHM_2$ = 393ps, $Intensity_2$ = 2.3%, $Shift_2$ = 275ps) on a constant background, into three components of positron lifetime and their relative intensities: $\tau_1 \pm \triangle\tau_1$, $\tau_2 \pm \triangle\tau_2$, $\tau_3 \pm \triangle\tau_3$, $I_1 \pm \triangle I_1$, $I_2 \pm \triangle I_2$, $I_3 \pm \triangle I_3$ (%).

III. RESULTS

The positron lifetime and their relative intensities measured in the Pd samples before electrolysis and after electrolysis at different time, as well as, annealing once more were listed in Tables 1—3 respectively, from which one can see that most data of valuable informations for samples of the same state are reproducible in the ranges of the experimental errors except very few ones resulted probably from the heterogenity of the sampled positions on the electrolysed material or other reasons. These discrepancies can be eliminated by averaging treatment.

Using the traping model and the approximation of no escaping probability from the trapping states, as well as the law of statistical error propagation, we obtained the formulae of the bulk lifetime τ_b and its deviation $\triangle\tau_b$ as follows:

$$\tau_b = 1/(I_1/\tau_1 + I_2/\tau_2) = 1/\lambda_b \tag{1}$$

$$\triangle\tau_b = \{[(\triangle\tau_1/\tau_1)^2 + (\triangle I_1/I_1)^2] \times (I_1/\tau_1)^2 + [(\triangle\tau_2/\tau_2)^2 + (\triangle I_2/I_2)^2] \times (I_2/\tau_2)^2]\}^{1/2}\tau_b \tag{2}$$

where the rate of annihilation of positron at free state λ_b in the bulk of condensed matter, was deduced by Dirac[2] and obtained a formula as follow:

$$\lambda_b = \pi r_o^2 c n \tag{3}$$

where r_o = classical electron radius, c = speed of light, n = electron number density at the place of positron annihilating, where N is the total number of electron in a

volume of V, and $n = N/V$ (1/cm^3); or

$$\lambda_b = 2 + 134\ n \qquad (4)$$

according to Brandt- Reinheimer formula of bulk annihilation rate considered enhancement effect on the free electrons in metals.

Table 1

Positron lifetime (ps) and relative intensities (%) in Pd before electrolysis

Sample	Spectrum	τ_1	$\Delta\tau_1$	τ_2	$\Delta\tau_2$	τ_3	$\Delta\tau_3$	I_1	ΔI_1	I_2	ΔI_2	I_3	ΔI_3
1	Pd0011	132	3	252	15	1936	329	78.97	4.11	20.77	4.00	0.26	0.14
	Pd0021	136	2	271	11	1888	890	81.06	2.64	18.80	2.61	0.14	0.04
2	Pd0022	136	2	278	12	1713	777	82.33	2.43	17.53	2.40	0.14	0.05
	Pd0023	137	2	282	11	2607	1847	82.86	2.09	17.03	2.09	0.11	0.03
3	Pd0031	137	2	281	12	2231	1509	83.95	2.14	15.95	2.13	0.10	0.03
4	Pd0041	137	2	276	13	1620	520	82.70	2.59	17.10	2.55	0.21	0.06

Table 2

Positron lifetime (ps) and relative intensities (%) in Pd after electrolysis

Sample	Spectrum	Time*	τ_1	$\Delta\tau_1$	τ_2	$\Delta\tau_2$	τ_3	$\Delta\tau_3$	I_1	ΔI_1	I_2	ΔI_2	I_3	ΔI_3
1	Pd0111D#	1h	151	3	306	16	1920	380	84.09	2.52	15.50	2.52	0.41	0.06
1	Pd0112D	3h	146	5	255	17	1127	155	83.72	6.15	15.61	6.05	0.67	0.14
1	Pd0113D	7h	149	3	297	16	1767	381	83.10	2.80	16.54	2.76	0.36	0.36
1	Pd0114D	16h	150	2	321	15	2327	660	86.06	190	13.63	1.88	0.31	0.04
1	Pd0115D	3d	150	3	314	17	1614	225	82.81	2.47	16.54	2.40	0.65	0.09
1	Pd0116D	21d	149	3	299	16	1487	156	79.15	3.12	19.97	3.04	0.89	0.11
1	Pd0117D	21d	154	3	321	22	1428	191	84.61	2.76	14.60	2.66	0.78	0.14
1	Pd0118D	21d	146	5	255	17	1300	112	71.90	6.73	27.05	6.65	1.05	0.12
2	Pd0121H#	5h	148	3	289	15	1740	507	82.14	2.98	17.62	2.94	0.22	0.06
2	Pd0122H	18h	149	3	291	15	2107	468	83.13	2.83	16.54	2.80	0.33	0.04
2	Pd0123H	4d	150	3	303	18	1550	220	83.16	2.82	16.23	2.75	0.61	0.09
3	Pd0131D	23h	150	3	297	22	1100	219	82.34	3.58	17.12	3.42	0.54	0.20
3	Pd0132D	26h	149	3	296	14	1680	400	80.71	2.90	18.96	2.85	0.33	0.07
3	Pd0133D	33h	151	3	295	22	1132	206	82.54	3.78	16.86	3.64	0.60	0.19
3	Pd0134D	40h	151	3	308	16	1730	446	83.50	2.60	16.18	2.55	0.32	0.07
3	Pd0135D	4d	150	3	304	16	1571	210	80.54	2.91	18.79	2.85	0.66	0.09
3	Pd0136D	21d	153	2	322	12	1644	141	82.15	1.73	17.02	1.68	0.84	0.07
4	Pd0141H	29h	149	3	307	16	1494	317	82.37	2.60	17.22	2.53	0.41	0.10
4	Pd0142H	26d	146	4	282	15	1384	145	75.33	3.92	23.78	3.82	0.88	0.12

* Time after stopping electrolysis # Spectrum number end D or H: electrolysed in D_2O or H_2O solution

The averaged values of the fitting results for the repeatedly measured spectra, $\tau_1 \pm \Delta\tau_1$, $\tau_2 \pm \Delta\tau_2$, $I_1 \pm \Delta I_1$, $I_2 \pm \Delta I_2$, and $\tau_b \pm \Delta\tau_b$ calculated using Eq.1 and 2, for the samples at several states: before and after electrolysing named Pd0 and Pd + D or Pd + H, respectively; after high temperature annealing($\geqslant$ 1100°C) named Pd + D + Anneal or Pd + H + Anneal; and after three- stage- annealing, i.e., 700 °C/24h(vacuum) + 1050°C/12h(Ar) + 700°C/5h(vacuum) + cooling slowly with furnace[5] named Pd[5]; were shown in Table 4, and its changing values were shown in Table 5.

Table 3

Positron lifetimes (ps) in Pd after electrolysis and high temperature annealing

Sample	Spectrum	$\tau_1 \pm \Delta\tau_1$	$\tau_2 \pm \Delta\tau_2$	$\tau_3 \pm \Delta\tau_3$	$I_1 \pm \Delta I_1$ (%)	$I_2 \pm \Delta I_2$ (%)	$I_3 \pm \Delta I_3$ (%)
1	Pd0211D#	117±1	321±6	1714±107	87.30±0.45	12.04±0.42	0.66±0.04
2	Pd0221H#	115±1	315±12	1573±181	87.26±0.88	12.04±0.83	0.70±0.08
4	Pd0241H	115±1	297±11	1431±166	85.30±1.13	14.06±1.07	0.64±0.09

Table 4

Mean values of τ_1, τ_2 and I_1, I_2 obtained from Table 1—3 and Ref.[5] and calcualted τ_b

Sample states*	$\tau_1 \pm \Delta\tau_1$ (ps)	$\tau_2 \pm \Delta\tau_2$ (ps)	$I_1 \pm \Delta I_1$ (%)	$I_2 \pm \Delta I_2$ (%)	$\tau_b \pm \Delta\tau_b$ (ps)
Pd0	135±2	273±12	81.98±2.67	17.86±2.73	148.7±3.5
Pd+D	149±3	299±17	82.56±3.08	16.88±3.82	163.8±4.4
Pd+H	148±3	294±16	81.23±3.03	16.27±2.97	165.5±5.7
Pd+D+Anneal	117±1	321±6	87.30±0.40	12.04±0.42	127.6±1.0
Pd+H+Anneal	115±1	306±12	86.28±1.00	13.05±0.95	126.1±1.5
Pd[5]	115±2	370±10	94.00±0.20	6.00±0.20	120.0±5.3

* Pd0: Pd sample before electrolysis; Pd+D and Pd+H: The Pd sample after been used as cathode for electrolysing D_2O and H_2O, respectively; Pd+D+Anneal and Pd+H+Anneal: The Pd+D and Pd+H after annealing once more at 1100°C; Pd[5]: The pure Pd sample annealed by three steps reported in Ref.[5].

Table 5

The changing values and their deviations of positron lifetimes (ps) and their intensities(%) calculated from Table 4 relative to the mean values measured in the Pd0 sample

Sample	$\Delta\tau_b$ (ps)	$\Delta\tau_1$ (ps)	$\Delta\tau_2$ (ps)	ΔI_1 (%)	ΔI_2 (%)	$\Delta\tau_b/\tau_b$ (%)	$\Delta\tau_1/\tau_1$ (%)	$\Delta\tau_2/\tau_2$ (%)
Pd+D	15.1±5.6	14.0±3.6	26.0±20.8	0.6±4.0	−1.0±4.7	10.2±3.8	10.4±2.7	9.5±7.6
Pd+H	16.8±6.7	13.0±3.6	21.0±20.0	−0.8±4.0	−1.6±4.0	11.3±4.5	9.6±2.7	7.7±7.3

In Table 5, we listed the values of and the changes in T_1 and T_2, 11, 12 and τ_b after electrolysis; and the changing rate $\Delta\tau_b/\tau_b$, $\Delta\tau_1/\tau_1$ and $\Delta\tau_2/\tau_2$, relative to the correspondent values of the Pd sample before electrolysis, using the data in Table 4; as well as, their statistical erroes calculated based on error propagating law.

IV. DISCUSSION

1. Positron lifetime in pure Pd polycrystalline

The first component of positron lifetimes in annealed pure palladium sheets may be attributed to annihilation in the bulk of Pd, because of the longer lifetime with small values of intensities, which may be due to insufficient source correction and annihilation in surfaces, according to Ref.[5]; and may be due to the contribution of crystal boundaries for the polycrystalline Pd, at which the positron trapping can not be neglected, according to our opinion.

In the present work, probably owing to the impurities, and/or, the insuffisent annealing, τ_b is about 127 ps, a little bigger than that of Ref.[5], 120 ps, which may be

more approaching to the bulk lifetime of positron in polycrystalline pure Pd without evident trapping centers except the crystal boundaries.

2.Volume expansibility of Pd after transition from α —PdH to β —PdH phase

From Table 5, we can see that $\triangle\tau_1/\tau_1 \approx 10\%$, which means the electron number density had decreased in Pd after electrolysis. There may be mainly three posibilities causing such a decreasing in electron number desity: (*a*) bulk effect (cubical expansion); (*b*) defect trapping effect; and (*a*)+(*b*). But our opinion is the (*a*), by reason of the following: From Eq.1, we obtain

$$\tau_1 = I_1\tau_2/(I_2\lambda_b - I_2) \tag{5}$$

It is obvious to see that $\triangle\tau_1$ only related to the changing in value of the bulk annihilation rate, τ_b, because I_1, τ_2, and I_2 after electrolysis have not evidently changed, i.e., close to constants, considered the statistical errors as shown in Table 5. And in which we find a approximation relationship:

$$\triangle\tau_1/\tau_1 \cong \triangle\tau_b/\tau_b \cong 10\% \tag{6}$$

Therefore, the changing rate of about 10% in τ_1, is only a bulk effect, but a defect trapping one caused by D or H filling into Pd under our experimental conditions. Furthermor, after anealing once more, the electronic structures in Pd can recover to ones of pure polycrystalline Pd. This would be a evidence for no micro crack created in our Pd+H and PH+D samples, because the crack would be irreversible defect and can not be annealed out. So, the 10% changing in τ_1 or τ_b, would be responsible for volume expansion. If we postulate that the positron is equally likely to be in the crystal, then, the volume expansibility of the Pd,

$$\triangle V/V \approx \triangle\tau_b/\tau_b \approx 10\% \tag{7}$$

But the approximation that the positron samples all regions of the crystal equally is clearly not valid, the positron will avoid the regions of high electron density around the cores, namely, at Bloch state, it is based on the theoretical calculation[6] to obtain

$$\triangle V/V \approx 1.5 \times \triangle\tau_b/\tau_b \approx 15\% \tag{8}$$

On the other hand, we find the following data about the crystal lattice of palladium with α - and β - phase[7], lattice parameters a (α - Pd) and a (β - Pd): a (α - Pd)=0.3891 to 0.3894 nm, a (β - Pd)=0.4027 to 0.4070 nm, a (β - Pd)/a (α - Pd)=2.5 to 4.5%.

Cubical expansion of the cell:

$$\triangle V/V = [V(\beta - \text{Pd}) - V(\alpha - \text{Pd})]/V(\alpha - \text{Pd}) \approx 11 \text{ to } 14\% \tag{9}$$

Compareing Eqs.(8) and (9), we find that the 10% of $\triangle\tau_b/\tau_b$ would corresponding to 11% to 14% of $\triangle V/V$, the volume expansibility expected for the formation of H- Pd and D- Pd compounds with the so- called β - phase, namely, transition from the α - phase (fcc Pd) to β (octahedronal interstitial) phase of PdH or PdD[7]. This kind of phase transition had been confirmed by the X- ray diffraction patterns of Pd cathode

used for D_2O electrolysis[8].

3. Pressure and cracks in Pd cathode during electrolysis

The pressure in the Pd had to be greater than 2.78×10^{10}Pa, to result in such a volume expansing as greater than 11%, based on the calculation using the compressibility of Pd[7]. During the off- equillibrium electrolysing compressing process of H or D into Pd, the pressure would be even higher according to the continuous increasing of doppler broadening parameter[9], but which may also be attributed to crack creating after reaching certain stress level in the lattices.

4. Positrons and atoms at interstitial sites

Combined with the PAS experiment, the EHP (Electrochemical Hydrogen Permeation) experiment had also been done. After stopping the electrolysis, the H and D atoms entered into the Pd lattices will mostly escaped out, and only a small portion of them reserved in as a result of the continuously escaping for a comparatively period of time, say a few days, during which the PLS did not changed evidently as shown in Table 2, although the atom number of H and D in the lattices did changed obviously in the light of our EHP data, which will be published else where. This may be due to the positron is not sensitive to the atoms at interstitial sites.

5. Behavior similarity of H and D

It is well known that the structures of H and D atoms are almost the same; and the behaviors of them, in most cases, are also very similar, except that the p- p nuclear fusion rate is very slow relative to the d- d one resulting from the nucleus structure of hydrogen, in which there is no any neutron at all. So, most people pay more attention to deuterium as precious fusionable material, but elbow hydrogen out the family of fusionable materials. In fact, hydrogen would be the most cleanest and the real inexhaustible fusion energy source material in nature, because it is the nuclear fusion reaction,

$$4{}_1^1\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2\,e^+ + 2\nu_e + 2\gamma \qquad (10)$$

to provide main energy that sets the stars ablaze, the sun shines, the earth evolves, and then the human being lives,..., regardless this reaction have not been realized on the earth up to date yet. Bur we would not give up the lofty ideal in energy science.

From the PLS result, it seems to be that the H and D atoms entering into the Pd lattices may result in similar changing in the electronic structure and/or defect structure, equal decreasing of the electronic number density, or, the same effects of defect creating or volume expanding.

In line with Ref.[10,11],; and our EHP results, the diffusion coefficients of D and H in Pd are in the same order of quantity, and the reserve ratio of them in Pd is about unit. It seems to be that the H and D atoms in the Pd would have a similar profile of concentration or a distribution of pressure, under the same experimental conditions.

This implys that the only difference of one neutron mass between H and D atom, will not effect the behaviors of them in Pd remarkably, the key factor determining the behaviors of them in Pd would be in the electricity of them; in other words, H would behave in similar ways as though it were D, and vice versa. Then, we may use the behaviors of H to analogize the D in Pd or other metals, in most case, except the behaviors of nuclear reactions. This may be of great importance in material science.

V. CONCLUSIONS

PLS of Pd samples filled galvanostatically with H and D were all the same if other conditions were maintained; and the changing rate in its first component τ_1 was about 10%, while the other components did not change distinctly after electrolysing H_2O or D_2O with Pd cathode; The PLS in the samples of Pd filled with D and H did not changed with the time after stopping the electrolysis, and could recover to ones in the polycrystalline pure Pd after been annealed once more.

These results suggest that the electron structures of crystal lattice and defects resulting from H and D filling into Pd are all the same; and that the changes in the positron lifetime parameters after electrolysis are responsible mainly for the volume expanding, but for crack creating; as well as, the positron may not be sensitive to the H and D atoms at the interstitial sites of Pd.

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