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# **ANOMALOUS THERMAL NEUTRON CAPTURE AND SUB-SURFACE Pd-ISOTOPES SEPARATION IN COLD-WORKED PALLADIUM FOILS AS A RESULT OF DEUTERIUM LOADING**

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## **ABSTRACT**

The process of thermal neutron absorption in the cold-worked Pd cathodes during electrolysis in NaOD/D<sub>2</sub>O solution under irradiation by Ultraweak Thermalized Neutron Field (UTNF) was studied. It was found that during deuterium loading the probability of thermal neutron absorption in a strained Pd is increased by a factor 8 compared to the unstrained (annealed) sample or sample where loading is not carried out. Symmetric separation of Pd isotope pairs of Pd<sup>108</sup>-Pd<sup>105</sup> and Pd<sup>110</sup>-Pd<sup>104</sup> occurring in the subsurface layer down to 500 Å depth in the cold worked Pd foil loaded with deuterium is observed. It is established that observed Pd isotope separation is solely defined by a strong plastic deformation (mechanical strain), induced by deuterium loading in Pd-matrix. The effect of Pd-isotopes separation is strongly enhanced under UTNF irradiation

## **1, INTRODUCTION**

If the phenomenon of Cold Fusion or Lattice Induced Nuclear Reactions (LINR) is really exist then the effects of nuclear interaction in crystalline lattice of metal deuterides should be sharply distinct of that in vacuum/plasma environment. Earlier it was shown that DD-reaction rate and branching ratios at low deuteron energies are strongly affected by crystalline lattice of some metals, including Pd [1,2]. However, the study of low energy deuteron interaction with Pd-metal is limited by the deuteron energy ( $E_d > 2.5$  keV) due to presence of nuclear Coulomb barrier, leading to dramatic decrease in the nuclear reaction yields at lower projectile energy. To rule out the Coulomb barrier influence on the nuclear interactions in solids we suggested to irradiate deuterated metal targets by the neutral particles, i.e. neutrons and study change in neutron capture cross-section in these targets [3]. As we showed in our previous works, the thermalized neutron capture cross-section in metals during electrolysis can be enhanced drastically due to specific inelastic scattering processes [4,5]. The phenomenon of increase in thermal neutron cross-sections is accompanied by a strong plastic deformation of irradiated non-equilibrium solids and leads to appearance of new unexpected properties in them. In order to observe structural changes and anomalous neutron capture the solid and UTNF should be satisfied following conditions [3-5]:

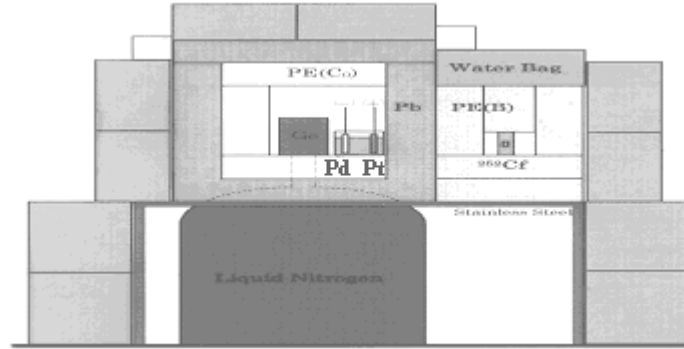
- High Excitation of the solid, which produces non-equilibrium optic phonon mode of energy  $E \geq \hbar\omega_D$ .
- Broad (“white”) neutron spectra (0.1-10 kT) overlaps the optic vibration frequency ( $\omega_D$ ) of excited system.
- Use an isotropic neutron field (not a beam) to allow neutron (with momentum  $p$ ) interactions with various directions of lattice phonon Debye wave vector  $k_D$ .

In present paper we studied the process of thermal neutron absorption and accompanying macro and micro-plastic deformation effects in the cold-worked Pd cathodes during electrolysis in NaOD/D<sub>2</sub>O solution under irradiation by Ultraweak Thermalized Neutron Field (UTNF).

## 2, EXPERIMENTAL TECHNIQUE

In the present work we are strictly concerned with UTNF, defined by a highly rarefied neutron gas (a low neutron density  $n \leq 10^{-3} \text{ cm}^{-3}$  or a low flux  $\Phi_n \leq 2 \cdot 10^2 \text{ n/s} \cdot \text{cm}^2$ ) with under-Maxwellian velocities (with mean energy  $\langle E_n \rangle \sim 1 - 10 \text{ kT}$ ) and isotropic angular distribution.

In order to create the neutrons field with flux  $\Phi_n \sim 200 \text{ n/s} \cdot \text{cm}^2$  the set up consisting of cavity with the  $\text{Cf}^{252}$  neutron source and the test sample surrounded with a large mass ( $\sim 1$  metric ton) of moderator (PE) is being used (**Fig.1**). The intensity of neutron source inside the cavity was  $2 \times 10^4 \text{ n/s}$  in  $4\pi$  solid angle. The mean neutron energy in the cavity in accordance to Monte-Carlo simulation was found  $\langle E_n \rangle \approx 80 \text{ meV}$ . The monitoring of neutron flux intensity inside the cavity was carried out by direct detection of thermal neutron ( $\text{B}^{10}\text{F}_3$  neutron counters) and by measurement (with HpGe detector) of the 2225 keV gamma-line intensity from neutron capture in moderator according to the:  $n + \text{H} \rightarrow \text{D} + \gamma$  (2225 keV). The electrolytic cell was placed inside the Pb-shielded cavity near the HpGe detector.



**Figure 1**

The cold-worked Pd-foils (purity 99.99 %) of 100  $\mu\text{m}$  thick were used as the cathodes. The samples of  $5.0 \times 2.0 \text{ cm}^2$  area were cut from a single foil sheet and then served as a cathode during electrolysis in  $1\text{N}-\text{NaOD}/\text{D}_2\text{O}$  solution (in the cell with separated cathode and anodic spaces [10]) at electrolysis current density  $j = 30 \text{ mA}/\text{cm}^2$  during 1-3 days at room temperature. After-electrolysis deuterium loading ratio in Pd samples was determined by thermal-desorption technique and constituted within the range of  $x=\text{D}/\text{Pd} \sim 0.80$ . Dislocation density in the initial (cold-worked, not annealed) Pd-foils was  $N_d=10^7 \text{ cm}^{-2}$ . After finishing of electrolysis, the macroscopic longitudinal bending ( $l$ ) (induced by the difference in molar volume of  $\text{PdD}_x$  phase across the electrode, developed during D-diffusion [6]) and the residual plastic deformation of the sample ( $\varepsilon_p$ ) were measured. It was established that after the electrolytic deuterium loading at natural neutron background condition those mechanical characteristics reach, in average,  $\langle l \rangle = 1.5 \text{ cm}$  and  $\langle \varepsilon_p \rangle = 3 \cdot 10^{-3}$  and dislocation density  $N_d = 1.5 \cdot 10^{11} \text{ cm}^{-2}$ . Under combined electrolysis and UTNF due to a stronger deformation at the same electrolysis current these parameters became much larger, so that  $\langle l_n \rangle = 5.0 \text{ cm}$  and  $\langle \varepsilon_p \rangle_n = 3.3 \cdot 10^{-2}$  and  $N_d = 3.8 \cdot 10^{11} \text{ cm}^{-2}$ .

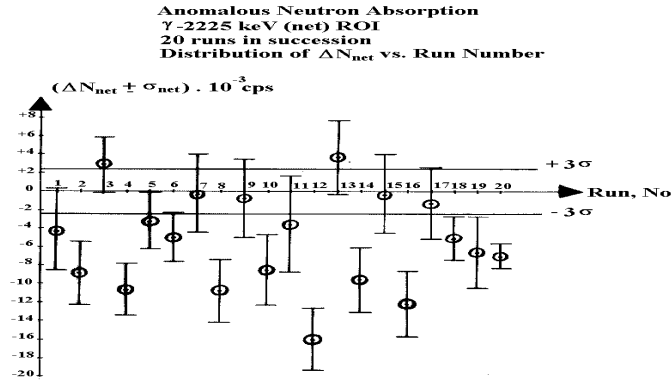
In order to determine isotope content and depth profile of Pd atoms in Pd samples the method of high resolution (1:2000) secondary ion spectroscopy (SIMS) was used. The CAMECA IMS 5f unit operating in the high-resolution mode allows to resolute all Pd isotopes (102-110) at the high confidence level and to separate Pd species from corresponding Pd hydrides/deuterides with similar mass, which were emitted in the secondary ion beam. Using SIMS device, the depth profiles (0.0 – 1600  $\text{\AA}$  from the surface) of Pd isotopes and the change in Pd sputtering rate versus depth were determined. In typical sputtering regime using  $\text{O}_2^+$  primary beam with current  $I = 10 \text{ nA}$ , diameter 100  $\mu\text{m}$  and energy  $E = 8.0 \text{ keV}$ , the sputtering rate was  $R = 4.1 \text{ \AA}/\text{s}$ . The error of Pd isotope concentration measurement at the depth  $h \geq 100 \text{ \AA}$  was less than 1.0 atomic%. In the subsurface layer with depth  $h < 100 \text{ \AA}$  this error is appear to be larger and reaches of about 3.0% due to the surface roughness, possibly results in decrease in a space resolution of device.

The probes of  $10 \times 10 \text{ mm}^2$  dimension were cut from the initial (unloaded and not annealed) samples and D-loaded Pd cathodes for SIMS analysis. For each sample, the five arbitrary chosen spots were analyzed. In order to estimate effect of internal strain on isotopic distribution of Pd atoms, the loaded samples after the primary analysis were underwent to a deep vacuum annealing ( $p=10^{-10} \text{ tor}$ ) at temperature  $t = 800 \text{ }^\circ\text{C}$  during 5 hrs. with following slow cooling (cooling rate  $v = 0.2 \text{ }^\circ\text{C}/\text{min}$ ). After this annealing, the bending and residual plastic deformation of the sample were almost eliminated and dislocation density dropped to  $N_d \sim 10^4 \text{ cm}^{-2}$ .

## 3, EXPERIMENTAL RESULTS

In the case of the strained Pd samples electrolysis (a) a statistic decrease of 2225 keV gamma line intensity in Foreground runs (with electrolysis) compared to the Background runs (  $j = 0$  ) has been established (Fig. 2). From 20 similar strained samples used in succession the negative difference between Foreground and Background was demonstrated in 18 cases, including 11 samples completely out of 3 sigma corridor , while positive difference with low significant level has been shown only for 2 samples. In the case of net ROI difference between Foreground and Background (after subtracting of continuum produced by inelastic scattering of fast neutrons from Cf -source ) the mean value  $\Delta N$  is strongly negative:

$$\langle \Delta N_{\text{net}} \rangle = - (5.95 \pm 0.75) * 10^{-3} \text{ cps.}$$



**Figure 2**

For annealed Pd samples (b) the situation with thermal neutron capture during electrolysis is completely different. The effect of thermal neutron capture for samples (b) was not observed, despite of the same broadening of 2225 keV line that is in (a) case. The number of positive and negative differences between Foreground and Background is approximately the same for this case. Moreover, all these values are inside of 3 Sigma corridor. The mean value of difference between Foreground and Background count for annealed samples was:  $\langle N_{\text{net}} \rangle = + (0.90 \pm 1.15) * 10^{-3} \text{ cps}$  , that are demonstrated a total absence of any significant difference between Foreground and Background count rate. It should be noted that statistically significant change in  $\gamma$ -line intensity is observed only for 2225 keV line in the case (a). For other intensive lines (for instance,  $^{40}\text{K}$  ,  $E_{\gamma}= 1458 \text{ keV}$ ) no any change in ROI upon the Foreground runs has been detected, neither in (a) nor in (b) cases. Thus, during the electrolysis (deuterium loading ) of the strained Pd samples the effect of enhancement of thermal neutron absorption is appeared due to capture of thermal neutrons by Pd cathode. In the case under consideration of about 5.5 % of thermal neutrons from total flux inside the cavity containing detector and cell with Pd cathode were captured by sample during electrolysis.

The data obtained allow to estimate the average effective coefficient of thermal neutron absorption increase ( $K_a$ ) in the strained Pd samples as follows:

$$K_a \sim \langle \sigma_{\text{th}} \rangle / \sigma_{\text{Pd}} = (1/n_S \times L_S \times \sigma_{\text{Pd}}) \ln[1/(1 - n_C)],$$

where  $n_S$ ,  $L_S$  are the concentration of Pd atoms and sample thickness (  $L_S = 0.01 \text{ cm}$  ), while under ln sign there is a ratio between the fractions of falling thermal neutrons and transmitted through the sample (with subtracting of absorbed part  $n_C$  of total falling flux). In the case of strained Pd samples (a) we obtain the increase in thermal neutron absorption probability  $K_a = 7.5$  taking into consideration an average thermal neutron cross section for Pd isotope mixture  $\sigma_{\text{Pd}} \approx 10.0 \text{ b}$ . Therefore, the probability of thermal neutron capture in a strained Pd under combined electrolysis and UTNF is 7.5 times larger compared to that for normal (unloaded) state as well as for Pd samples with no internal strain.

Depth profile concentration for Pd isotopes showed that for electrolyzed samples with residual strain (with and without UTNF irradiation) in a thin sub-surface layer of 500 Å depth, the significant deviation of 104, 105, 108 and 110 Pd isotope masses from their stoichiometric values (natural isotope ratios) is observed. At the same time, the changes in 102, 106 and 107 Pd mass could not be considered as noticeable. In the Fig.3 (a-c) the profiles of 104, 105, 108 and 110 Pd isotopes for electrolyzed and annealed samples with subtracting of similar data obtained for initial sample are presented. For the sample underwent to electrolysis in the natural neutron background condition (Fig.3a) the traces of separation of Pd<sup>108-105</sup> and Pd<sup>110-104</sup> isotope pairs are observed down to 200 Å depth. It is well seen that Pd- layer with  $h < 50 \text{ Å}$  depth is “enriched” by heavy isotopes (108 and 110), while at the depth of  $h > 50 \text{ Å}$  the inversion of isotope

separation takes place, so that the layer  $50 < h < 200 \text{ \AA}$  is enriched by light isotopes (104 and 105) and depleted with heavy ones (108 and 110).

In the sample after combined electrolysis and UTMF (Fig.3b) the isotope separation effect has a sufficient significance level. In this case, the fraction of enrichment with heavy Pd-isotopes and corresponding depletion by light Pd-isotopes in  $h < 50 \text{ \AA}$  sub-surface layer is reached to 10-12 %. Furthermore, the changes in heavy (108,110) and light (104,105) Pd- isotopes profiles are quite symmetric following the sample's depth profile. In the more detail picture (Fig.4), the data on concentration of 104,105, 108 and 110 isotopes are normalized to that for  $\text{Pd}^{106}$ -isotope that is practically unchangeable within the total depth. As seen, the symmetry of isotope separation is clear expressed for the pairs with the masses 108-105 and 110-104, respectively.

The effect of Pd-isotope separation (Fig.3 a,b,) was completely eliminated by the vacuum annealing of electrolyzed sample, i.e. by elimination of internal mechanical strains in it. As seen from the Fig.3c, the statistically significant values of differences between the Pd-isotope concentrations for annealed (Fig. 3b) and initial samples have not been observed within the total depth profile taken for detection. The last fact shows that observed isotope changes in the electrolyzed samples (Fig.3a,3b) cannot be explained by nuclear transmutations, since the transmutation effect supposed to be independent on sample annealing.

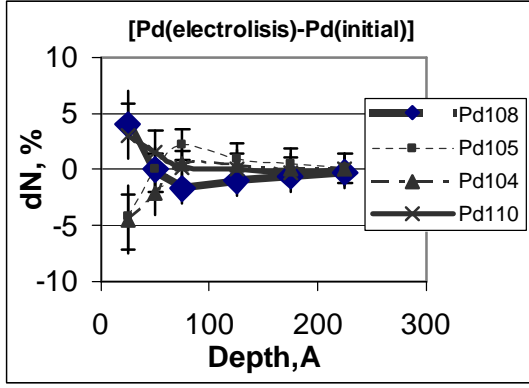


Figure 3 a

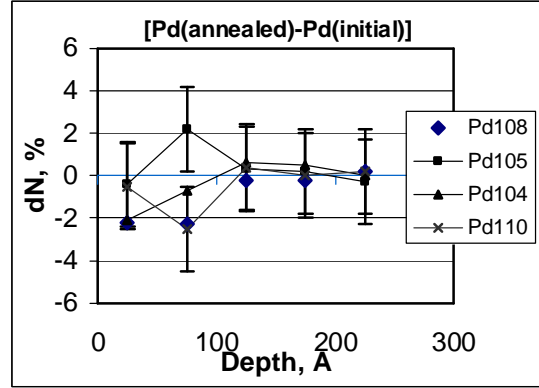


Figure 3 c

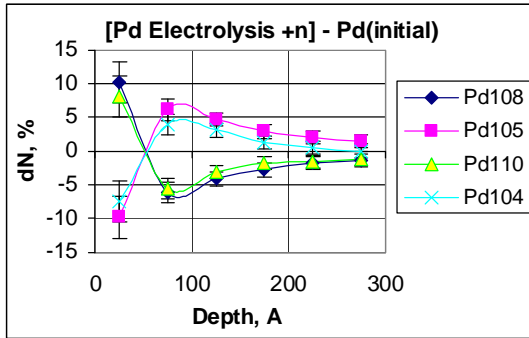


Figure 3 b

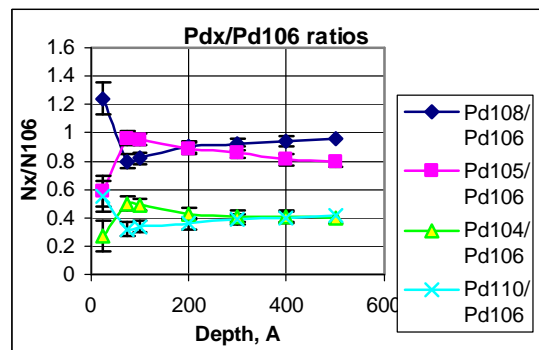


Figure 4

#### 4, DISCUSSION AND CONCLUSIONS

The mechanism of anomalous neutron absorption and energy conversion in plastic deformation in metals under H/D loading is just described elsewhere [4,5]. Here we consider possible reasons of Pd isotope separation in the deformed Pd sample (Fig. 3a) under deuterium loading. Since, on average, at the depth  $h > 100$  A the 108 isotope concentration is decreased by 5.0 %, while the 105 isotope concentration is increased by the same value, respectively, then the factor of full enrichment can be calculated as [7]:

$$A = \frac{N_f / (1 - N_f)}{N_T (1 - N_T)} \quad (1)$$

where  $\langle N_f \rangle = 0.265$  – is the mean concentration of Pd<sup>105</sup> and  $\langle N_T \rangle = 0.225$  – is the mean concentration of Pd<sup>108</sup>, and then  $A_1 = 1.24$ . Similarly, for Pd<sup>110</sup>-Pd<sup>104</sup> isotope pair the eq. (1) gives  $A_2 = 2.55$ . In order to explain these enrichment factors, let us consider a diffusion-induced isotope separation representation. In this model we assume that during deuterium overloading in the cold-worked Pd foil, the Pd-atoms in the sub-surface layer might self-diffuse through the metal/vacancy interfaces. In this assumption the heavy isotopes (108 and 110) will have tend to seize in the vacancies of crystalline lattice, while the light isotopes (104 and 105) would be travel easier to the surface, keeping higher mobility. As a result, the sub-surface layer with the depth  $h > 50$  A would be effectively enriched with the light Pd-isotopes and depleted with the heavy ones. Furthermore, the SIMS yield of light Pd isotopes in this consideration would be larger than for heavy Pd isotopes because at the same parameters, the surface binding energy  $U_s$  for the mobile light isotopes will be lower than that for heavy ones (captured and bound to vacancies). The factor of isotope-separation in the diffusion method is given as follows:  $\alpha = (M_2/M_1)^{1/2}$ , where  $M_2$  and  $M_1$  are the mass of the heavy and light isotopes, respectively. For the 108-105 and 110-104 Pd-isotope pairs these factors are  $\alpha_1 = 1.0142$  and  $\alpha_2 = 1.0284$ , respectively. Since the factor of a full enrichment (1)  $A = \alpha^s$  (here  $s$  – is a number of stages of the separation process), then the numbers of stages for 108-105 and 110-104 isotope separation ( $A_1$  and  $A_2$  derived from eq.1) are determined as  $s_1 = 16$  and  $s_2 = 33$ , respectively. Assuming for simplicity that minimal distance between vacancy inter-layers is determined by PdD<sub>x</sub> lattice parameter ( $a_0 = 3.89$  A), the total minimal thickness to provide observed diffusion-induced isotope separation can be expressed as  $R = 2 a_0 s$ . Then, we obtain  $R_1 = 117$  A and  $R_2 = 257$  A, respectively or the mean self-diffusion path of Pd atoms toward the surface ranging of  $120 < R < 260$  A.

However, in the near-the-surface Pd layer of  $h < 50$  A depth, adjoined directly to the metal-vacuum interface, the character of isotope separation is drastically changed compared to that at  $h > 50$  A depth. As seen in Fig. 3 a,b the isotope separation curve changes its sign, so that heavy Pd–isotope

enrichment and corresponding light isotope depletion are occurred. In this case, the magnitude of isotope separation is several times larger than at the depth  $h > 50$  Å. The corresponding values of full enrichment ( $A$ ) at the near-the-surface layer ( $h < 50$  Å) for 108-105 and 110-104 Pd-isotope pairs are  $A_1 = 3.05$  and  $A_2 = 4.55$ , respectively. These large  $A$  values, in terms of self-diffusion-induced Pd-isotope separation model should request the large numbers of stages ( $s_1=80$  and  $s_2=54$ , respectively) or the long diffusion paths:  $R_1=620$  Å and  $R_2=420$  Å, respectively. We, therefore, need to assume that in the shallow near-the-surface layer, the more efficient sources of isotope separation should operate. Indeed, the screw dislocations, dislocation loops (Frank-Reed sources) or spiral steps generated during intersection of screw dislocations with the surface, can serve as such efficient sources of Pd-isotope separation. Due to rotation of these linear defects with the sub-sound velocity accompanying by a mass transfer (Pd atoms move), those sources could serve as the efficient “micro-centrifuges” for isotope separation. In this case, the single separation factor  $\alpha$  for this micro-centrifuge would be determined as [7]:

$$\alpha = \exp \left[ \frac{(M_2 - M_1)v_s^2}{2RT} \right] \quad (2)$$

where  $v_s$  – is an effective rotation velocity in the dislocation source (taken as a half of sound velocity);  $R$  – is the universal gas constant and  $T$  – is the effective temperature of the dislocation source. In accordance with (2) at  $T=300$ K the separation factors for 108-105 and 110-104 isotope pairs are  $\alpha_1 = 2.6$  and  $\alpha_2=6.5$ , respectively. Thus, in the dislocation “micro-centrifugation” assumption, the Pd-isotope separation would be very efficient and will be achieved by the one separation stage ( $A = \alpha^s$ ,  $s \leq 1$ ) within the depth  $h < 50$  Å.

In contrast to diffusion-induced separation, upon this “centrifugation” the heavy isotopes would be moved to the outer space of the centrifuge (dislocation source), while the light ones concentrated at the inner part of the source, i.e. captured by dislocation cores. As a result, the surface of the sample would be enriched by the heavy (moveable) Pd-isotopes and depleted with light ones, bound to dislocation cores.

In summary, we showed that electrolytic loading of Pd with deuterium is accompanied by anomalous thermal neutron capture and strong near-surface plastic deformation of Pd cathode. The deformation process is a cause of the change in the isotope distribution in the sub-surface layer of Pd-cathode.

It should be noted that in the scope of the observed effect of Pd isotope separation, the results on “nuclear transmutations” obtained by SIMS technique in many cases can be explained in terms of the strong internal strain stored in Pd under deuterium loading. Furthermore, even the NAA method in view of discussed topic would not be free from the errors on the impurities detection in PdD<sub>x</sub> cathodes. If the thermal neutron cross-section had increase in the sites of internal strain concentration, then the NAA would show the increase in impurities concentration in these sites.

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