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HEAT MEASUREMENTS AND SURFACE STUDIES OF PD WIRES AFTER BEING EXPOSED TO A H2 GAS-LOADING SYSTEM IRRADIATED WITH A YAG FREQUENCY DOUBLING LASER

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Abstract: This study involved excess heat triggering attempts with a YAG frequency doubling laser (λ=532nm) used to irradiate palladium hydrides with different gas-loading ratios. The results showed that experiments using laser stimulation produced no significant excess heat evidence. However, on the surface of Pd sample there were some new elements including Ag and Cd. These were found in localized sites by SEM and EDS analysis.

Key words: H/Pd system gas-loading, YAG frequency doubling laser, excess heat triggering

1. Introduction

Laser stimulation is a potentially useful method in excess heat research. In 2003, D.Letts and D.Cravens[1] reported a method for generating highly reproducible and appreciable excess heat from deuterated palladium electrodes in heavy water electrolysis. Then V. Violante[2] and K. Sinha[3] modified and repeated the Letts experiment in 2005 and 2006. A gas-loading system can reach a relatively high temperature with the same amount of energy than in the electrolysis system due to the lower heat capacity of gases. Hydrogen has often been thought of as a control in cold fusion experiments. It is not generally accepted that the H/Pd system can produce any abnormal phenomenon. But does the hydrogen always behave like that? What would happen when ambient conditions are changed? This report concerns the use of a YAG laser with frequency doubling. Its wavelength is 532 nm. It was used to irradiate a series of palladium hydrides with different loading ratios (x =[H]/[Pd]= 0, 0.2, 0.3, 0.4, 0.8) . After laser stimulation, all of the samples including the original Pd were studied with scanning electron microscope (SEM) for surface topography and for elemental analysis with an energy dispersive spectrometer (EDS). Dash et al [4,5] found excess heat and new elements on the surface of a Pd cathode after heavy water electrolysis. But we are not aware of any such laser triggering experiment in a H/Pd gas-loading system.

2. Experimental

2.1 Apparatus and materials

Figure 1 shows the schematic of the experimental system. In which the reaction vessel is a glass flask with the dimension of Φ=6cm and h=26cm, with capacity roughly 750 cm^3. Palladium wire (99.98%Pd) was obtained from the 621 Institute of Aero-astronaut Ministry of

China. Its size was $\phi 0.01 \times 50$ cm and volume about $4 \times 10^{-3} cm^3$.

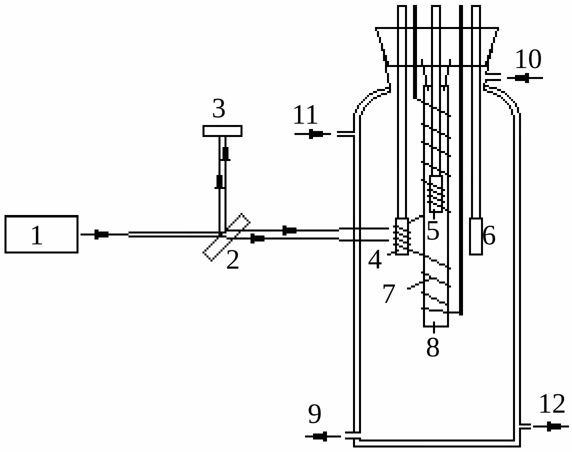


Figure 1 The schematic of our H/Pd gas-loading and laser triggering system. In which: 1-YAG laser, 2-3/7 reflection mirror, 3-laser power meter, 4、5、6-Pt100 thermometer, 7- Pd wire, 8-ceramic tube frame, 9-connection to the vacuum system, 10-connection to a super-pure hydrogen gas generator, 11、12- inlet and outlet connections to the water circulation system

Before the experiment the Pd wire was immersed in acetone and ethanol respectively for 20 minutes, and then cleaned by distilled water to get rid of impurities on the surface. Afterwards the wire was wound on a ceramic tube frame. Three Pt100 resistance thermometers were put inside the flask. One of them was for reading the temperature of the Pd wire that was irradiated by YAG laser. Another one represented the temperature of the Pd sample that was not irradiated by the laser. The third Pt100 thermometer was for recording the gas temperature inside the flask. The function of three-seventh reflection mirror was for monitoring the change of laser power. The reaction chamber was evacuated using a mechanical pump (Chengdu Southlight 2X2-4B) and a molecular turbine (Asslar PFEIFFER D-35614). The pressure of the chamber was read by a vacuum gauge (PFEIFFER TPG-262). The hydrogen gas was generated by a super-pure hydrogen generator made by Beijing Huayuan Gas Company. The purity of the H_2 was about 99.999% after a long working time. The loading ratio was determined by the resistance of the Pd wire (four-line method to measure the voltage and the current between the Pd wire, then calculate the resistance). From the correlation between the R/R_0 and x=[H]/[Pd], we can obtain the loading ratio of the Pd wire. The DC power supply for heating the Pd wire was model WYJ-302B made by Apple Electronic Apparatus Limited Company, Shanghai, China. A data acquisition system (Keithley 2700) made in the USA was used for reading the voltage and current in the Pd circuit. Four Pt100 resistance thermometers, including the thermometer that recorded the room temperature, were monitored. Laser wavelength (λ) was 1064nm, after frequency doubling, it became 532nm, which could pass through the glass-made flask. The laser has four types of pulse frequency (1, 5, 10, $15s^{-1}$) and four kinds of working voltages (750, 800, 850, 900V). Its maximum power was 2.0W.

An important feature of this gas-loading apparatus is its water circulation system. It can keep the temperature in reaction chamber from fluctuating due to changes in ambient temperature. So the temperature of the water circulation system should be set higher than room temperature. Here 35±0.5℃ was chosen.

In order to characterize surface topography and microchemical composition, the Pd wires were taken out of the experimental chamber and examined with a SEM and an EDS after hydrogen gas-loading into Pd, and laser irradiation. The SEM model was ISI-SS40 equipped with an EDS, OXFORD model 5565.The area of the detector window was $10mm^2$. Its resolution was 138 eV. The detector was coupled with ISIS software (the name of the specific program was SEMQuant) that estimated the elemental composition of a spot or area on the sample based on the X-ray spectrum. The more X-ray counts that were acquired, the more accurate that the X-ray analysis turned out to be. The accelerating voltage was set at 20 kV for all characterizations.

2.2 Experimental methods and results

2.2.1 Laser stimulation of pure palladium wire to determine background

In order to determine whether an abnormal phenomenon does exist in this system, the normal behavior should be confirmed in advance. That is, the background stimulation effect for the pure Pd wire (x=0) has to be tested before the experiment. Firstly, the system was pumped to a lower vacuum level (~2.0Pa). Then a series of laser beam powers and frequencies were applied on a section of Pd wire (about 9mm in length) for one hour. The temperature of the wire read by a Pt 100 thermometer was increasing gradually and then it reached steady state. Then the laser was turned off, and the heating coefficient (k) was calculated by the following formula: $k = \Delta T / \Delta P$ (℃/W) , where ΔT is the steady state temperature difference before and after the laser was turned on; ΔP refers to a change in laser power. But here it is the input laser power. In the laser working model of 900 V and pulse frequency of 15 s^{-1}, the heating coefficient in this system is 117±10℃/W.

2.2.2 Laser Stimulation of Pd hydride formation with different loading ratios

A laser beam was turned on and off repeatedly on the same spot of the same Pd wire for the same period (1 hour), but the loading ratio of the wire was different each time. The loading ratios of 0.2, 0.3, 0.4 and 0.8 of hydrogen in palladium were taken into account. As a typical result, the corresponding change of palladium temperature with different loading ratio when the laser irradiated the Pd sample are shown as in Figure 2.

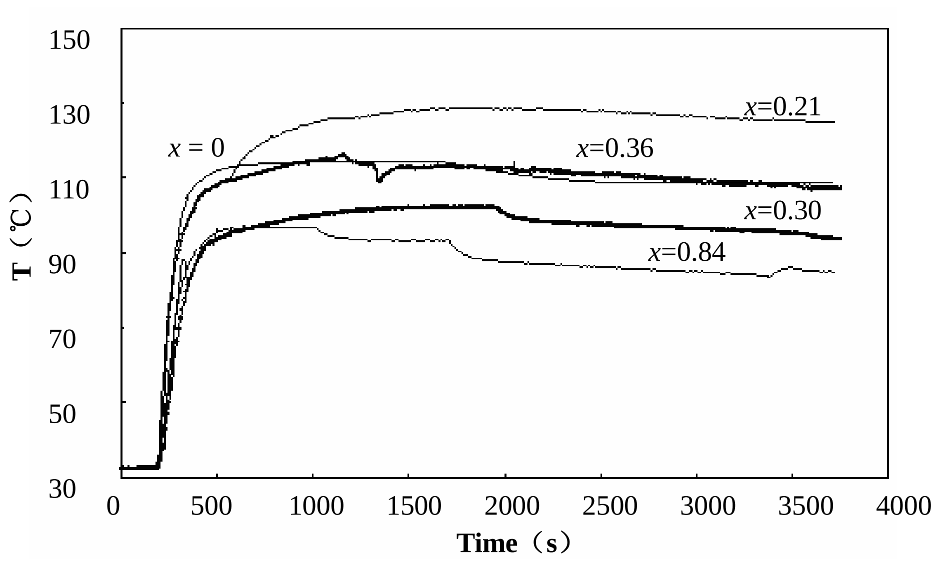
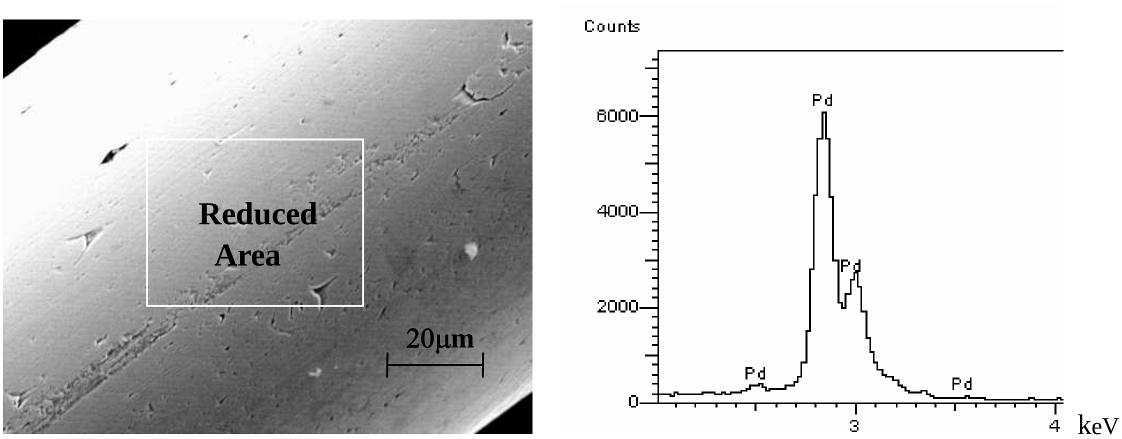


Figure 2 Temperature of a Pd wire with various loading ratio after irradiation with a YAG laser (Power = 0.70W, V = 900 V, Pulse Frequency = $15s^{-1}$). There is no significant

excess thermal power in this data

2.2.3 Topography and surface composition of Pd wire after gas-loading and laser irritating

The Pd wires were examined by SEM and EDS after hydrogen gas-loading, along with an as received Pd wire which served as a control. The samples were not cleaned before each examination. New surface topographical features with concentrations of unexpected elements, for example Ag and Cd, appeared after gas-loading. The Pd wire topography and microchemical composition before and after H gas-loading are given in Figures 3、4 and 5.

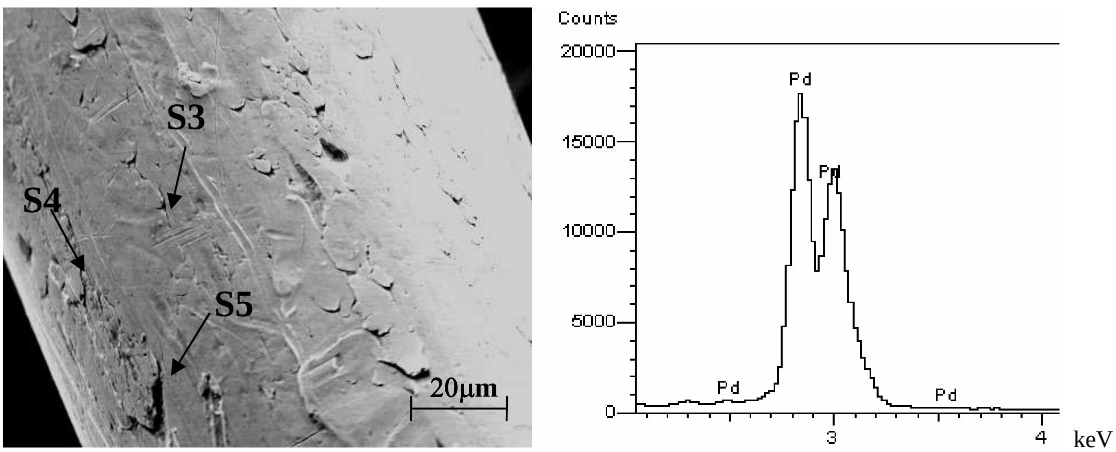


(a) (b)

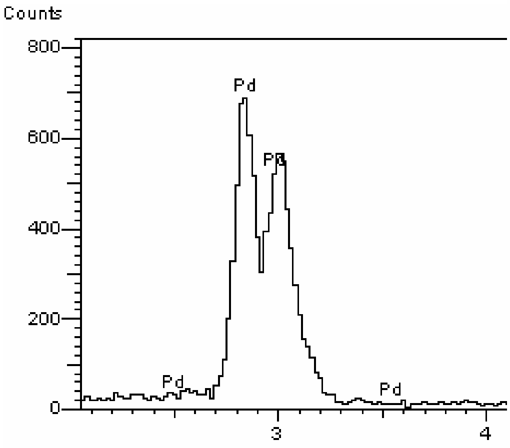
(a) An image of the surface of an as received palladium wire

(b) The spectrum from the reduced area in the image of palladium wire. The pits in the reduced area contained impurities such as Si, but there was no Ag or Cd..

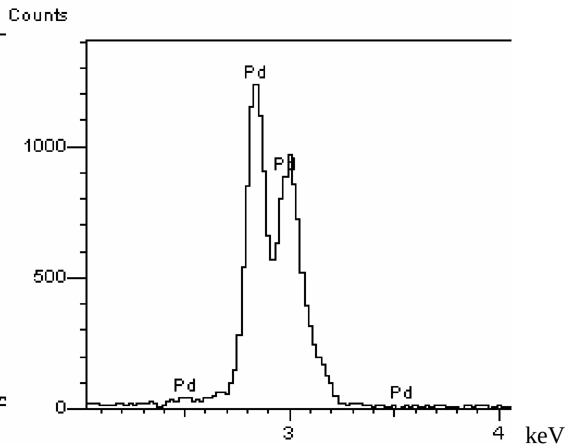
Figure 3 The image and spectrum of Pd original sample before H_2 gas-loading



(a) (b)



(c)



(d)

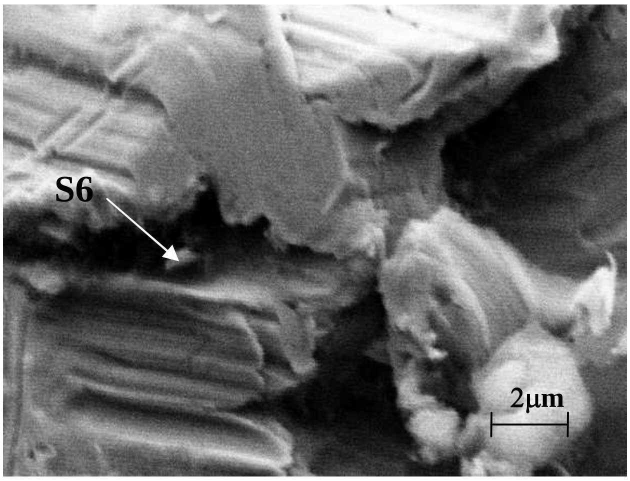
(a) The image of the surface of Pd sample after H_2 gas-loading

(b) The spectrum of spot 3 in above image

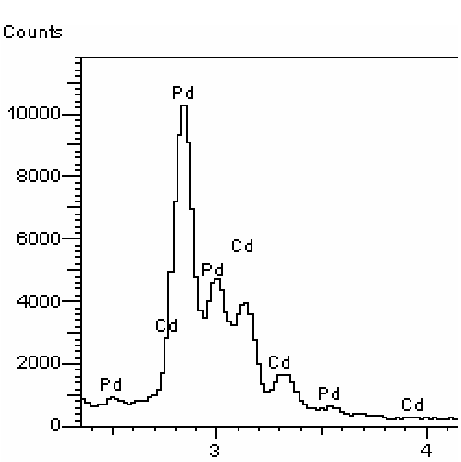
(c) The spectrum of spot 4 in above image;

(d) The spectrum of spot 5 in above image.

Figure 4 The image and spectrums of surface of Pd sample after H_2 gas-loading 10 times



(a)



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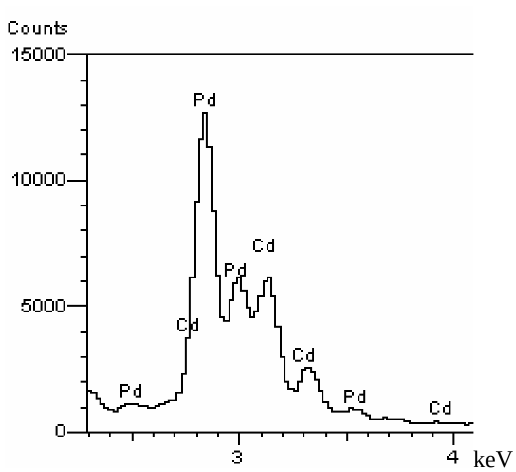

(c)

(a) An image of the surface of a Pd wire after H_2 gas-loading more than 20 times

(b) The spectrum of s6 in above image taken on Mar 23, 2007

(c) The spectrum of s6 in above image taken on Mar 26, 2007

Figure 5 An image and spectrums of surface of Pd sample after H_2 gas-loading

3 Analysis and discussion

3.1 Variation of excess heat with the loading ratio of Pd hydride and pulse frequency of a laser

From Figure 2 we can see that when the loading ratios were between 0.2 and 0.4, the Pd wire sometimes showed an exothermic behavior when it was irradiated with a YAG laser. In 60 experiments 13 of them produced exothermic behavior and their loading radios were located within this range. When the ratio was more than 0.8, the system had no exothermic behavior. It can be concluded that in this Pd/H system, a relatively low loading ratio can produced exothermic behavior. But in these 13 cases there were 10 times experiments which showed excess heat in the higher pulse frequencies of the laser. The explanation for this phenomenon is not clear at present.

3.2 Rough estimation for excess heat in the experiment

When the laser beam passed through the glass wall, there was a spot on the surface of Pd sample. The volume of Pd being irradiated was only about one fifth (9mm)of the whole wire. The number of Pd atoms is about 1.0×10^{20}. If they all combined with hydrogen atoms to form palladium hydride they would release heat of formation of about 6.4 joule, which corresponds to about 6.4×10^{-20} for each PdH. When the loading ratio is 0.3, as in our experiment for example, there should be 3.0×10^{19} hydrogen atoms dissolved in the bulk of palladium lattice, that is to say they would release 1.9 joule when these hydrogen atoms combined with Pd. But we measured 232.4 ± 0.3 joules heat released from the experiment that had the most significant exothermic behavior, which corresponds with 7.73×10^{-18} joule per atom Pd. Obviously the heat we get in experiment is about 130 times more than that released in the formation of a PdH_x (x=0.3).

However, the of temperature of the Pd wire varied greatly (more than ±10℃) at high temperature (T >100℃) duo to the instability of the laser power output. Also some H_2 was released from the Pd bulk when it was being irradiated. Because of the large uncertainty in the measurements, we will not make claims of excess heat in this paper.

3.3 Surface topographical and composition change before / after the Pd was gas-loaded with H

3.3.1 *Surface topography change*

In Figure 3(a) and Figure 4(a) (same magnification) the surface feature of Pd sample was obviously different before and after it had absorbed some certain amount of hydrogen gas. The surface became coarser than before gas-loading. There were some holes and cracks formed when the hydrogen was absorbed into the palladium lattice. This made hydrogen loading into palladium easier afterwards. That is to say, it would take less time (at least one fourth) that taken in the first time.

3.3.2 *Surface microchemical composition change*

The original Pd wire was checked by SEM and EDS before gas-loading. Eight spots were chosen for the test. All of the results showed that there nearly was 100% Pd in the sample. (see Fig.3(b)). After loading H into Pd, silver appeared in localized places like dark pits and dark cracks. The highest composition of Ag was as high as 12.79% (Fig.4 (a)s4, (b)). When the sample experienced gas-loading for longer time, for example more than 20 times, cadmium appeared in the place where Ag was usually found before. Furthermore, the concentration of Cd became higher as the time increased. The data showed that the concentration increased from 10.48% (Fig.5 (b)) during the time it was checked at beginning to 12.62% (Fig.5(c)) three days after. The detailed results could be referred in Table 1.

Table 1 The concentration of new elements on the Pd surface after H gas-loading

New element	*Element Content(%)*	*Sigma (%)*	*Atomic Ratio*	
			Ag/Pd	*Cd/Pd*
Ag	5.12	0.14	0.23	-
Ag	8.20	0.91	0.29	-
Ag	12.79	1.04	0.26	-
Cd	10.48	0.27	-	0.31
Cd	12.62	0.24	-	0.41

4. Conclusions

The following are possible conclusions which can be drawn from the experiments above:

4.1 A high loading ratio may not be a necessary condition for excess heat production. There may be an optimum ratio for each specific experimental condition.

4.2 The results of SEM and EDS reveal new elements on the palladium surface, such as silver, cadmium. These elements are clustered in localized, microscopic surface features such as cracks or pits. These elements were not found on the wires before loading.

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