

TRITIUM GENERATION DURING ELECTROLYSIS EXPERIMENT

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Introduction

In continuation of the earlier R&D work carried out in connection with the investigations for electrochemically induced fusion of deuterons using palladium cathode and platinum anode, a series of experiments was carried out. The following is a summary of results and observations for two such experiments:

PDC-II Experiment

Start of the expt. 10.7.89 - Conclusion of the expt. 25.7.89.

- a) Cathode - Palladium cylinder
 - i) Thickness - 0.45 mm
 - ii) Surface area - 6.37 cm²
 - iii) Volume - 0.143 cc
 - iv) Weight - 1.7 g
- b) Brief history of the palladium cathode

— A cylindrical type of palladium cathode was obtained and it appears that this palladium cylinder had not been used earlier for any tritium work. However, it was used in the analysis of the hydrogen gas samples and hydrogen purification work.

— Palladium cylinder of 1 cm length was used.

— The palladium cathode was spot welded to a platinum rod.

— The cathode was cleaned by degreasing, using solvents like acetone and was subjected to heat treatment at 300°C under vacuum for 2 hours.

— The anode was platinum gauze of area 25 cm².

Cell and Accessories

The cell of about 100 ml capacity was made of quartz. The Pyrex glass lid was provided with cones for introducing thermometer, cathode, entry port for sparging solutions with pure argon gas and vent for liberated gases namely deuterium, oxygen and D₂O vapour for quantitative collection.

— The D₂O vapour collection: The evaporated heavy water from the cell was refluxed back into the cell with a water condenser and the vapour that escaped from the condenser was collected in a moisture trap which was kept cooled with ice.

— The argon, deuterium and oxygen were passed through a column of catalyst, which recombined deuterium and oxygen back to D₂O.

Note: In this experiment, the gases that are emerging after the recombination step were passed through a water trap without further provision for recombination over copper oxide column.

— For temperature measurement, a calibrated thermometer was used.

— Electrochemical measurement: The galvanostatic power source with provisions for current pulsing was used. Terminal voltage was measured by a digital panel meter.

— Materials used in the experiment:

— Heavy Water: Nuclear grade heavy water was used in the cell for experiments. The isotopic purity was 99.87% with an initial tritium content of 170 dpm/ml. ($0.076 \times 10^{-3} \mu\text{Ci/ml}$).

— Electrolyte: Electrolyte was prepared 0.1 normal with respect to LiOD by using E. Merck grade lithium metal, and 60 ml was used for experiment.

— IOLAR-2 grade argon was used throughout the experiment as carrier gas.

— The cell was cooled by an externally located fan.

Tritium Measurement

— Tritium counting was carried out using LKB system Model 1215, RACKBETA – II system.

Sampling

— Samples (2 ml) were withdrawn from the cell during the experiment from time to time to assess the tritium content.

— Counting procedure: Aliquots from the above samples have been drawn and added to 'Instagel Cocktail' with a total volume of 10 ml for counting the tritium. Known amounts of tritiated water from NBS standard cells were taken into 10 ml of Instagel as reference. The blank sample for tritium was also prepared in Instagel with tritium free water obtained through ground water. Along with these background samples, counting was also done simultaneously for samples drawn from the double distilled water used for diluting and making up the samples for counting. Where interesting results were obtained, the full tritium spectrum was obtained and compared with the NBS standard tritium samples; when the samples gave significant activity, known amounts of the samples were distilled and the water distilled was taken for counting.

— During the electrolysis the cell level was maintained at a constant volume of 60 ml by periodically adding pure D₂O as mentioned above. Also, the alkalinity was maintained at 0.1 N by addition of LiOD from time to time.

Electrolysis

The following electrolysis procedure was adopted for the experiment. In the beginning, the electrolysis was continued at a constant current (40 hrs). Later the electrolysis was conducted using pulsing technique of varying current. It may be noted that the pulsing was carried out in this particular experiment only during the day time and in the night time the electrolysis was at a constant current. The details of the electrolysis parameters such as the values of constant current, pulsing current, duration and also the tritium values obtained during the experiment are given below:

From 12.7.89 to 25.7.89 the electrolysis was conducted in the nights with constant current of 1 amp and pulsing of the current was conducted during the day time.

Degassing Procedure

The following procedure was used to heat the electrode to recover the deuterium and tritium.

At the termination of the electrolysis the cathode was transferred to a quartz heating tube and was connected to a vacuum assembly. The moisture was removed from the electrode surface by heating to 80 - 110°C and condensed in a cold trap. After condensing the moisture, oxygen and nitrogen gases were recovered by standard getters. The electrode was gradually further heated and the gas released was purified and absorbed in a pyrophoric uranium trap. The electrode was maintained at 550°C for 2 hours till no further release of gas took place. Deuterium gas was released from this pyrophoric uranium trap, diluted with about 2.5 l of hydrogen and was converted into water by circulating through heated CuO bed. This water was taken for tritium counting.

Observations: Table IB

— On 11.7.89 between 11.55 and 12.20 hrs. there was power breakdown for 25 minutes.

— The first sample, PDC-II.1, was collected after 75 amp.hr. for tritium assay. It gave 1.59 $\mu\text{Ci/ml}$ of D_2O . The total volume of D_2O in the experiment at this time of sampling was 60 ml. The tritium activity accounted would be 95.4 μCi . It may be mentioned that the total D_2O (cell volume of 60 ml and make up volume of 40 ml) works out to be 100 ml. The excess tritium that has been produced at the end of 75 amp.hr. electrolysis works out to 1.25×10^4 times at this stage.

— The second sample was withdrawn at 235.65 amp.hr. and the assay of the sample showed that the activity per ml of the cell came down to 0.76 $\mu\text{Ci/ml}$. With a view to examine the behaviour of the cell, the experiment was continued up to 433 amp.hrs. and intermittent samples were taken.

PDC-II.3 (273.3 amp.hr.), PDC-II.4(381.5 amp.hr.), PDC-II.5 (433.32 amp.hr.).

— On 26.7.89 at about 1015 hrs. the lid of the electrolytic cell was thrown out along with the anode and thermometer. The experiment was stopped and a new lid was put with the cathode inside the cell. Oxygen and argon mixture was bubbled through the cell and a final sample PDC-II.5 was taken on 28.7.89 and was assayed for tritium activity (0.31 $\mu\text{Ci/ml}$.)

Observations: Table IC

- The total activity recovered is 55.52 μCi during the electrolysis and after the stoppage of electrolysis 0.71 μCi was recovered from the vapour condensate and deoxo- recombination trap. Electrode degassing yielded 0.03 μCi and in all 56.27 μCi were recovered.
- Total input of tritium activity from (60 ml cell volume + 196 ml make-up volume) 256 ml is 0.02 μCi .
- In all out of 256 ml of D_2O used, 132 ml of D_2O was recovered and accounted for at the end of the experiment.

In conclusion, it may be pointed out that at the end of 75 amp.hrs the electrolysis generated about 95.4 μCi excess tritium (12500 times the input). However, at the end of the electrolysis, that is, after 433.32 amp.hrs. the total excess tritium recovered works out to be 56.25 μCi .

PDC-III Experiment

Start of the Expt. 6.9.89. Conclusion of Expt. 14.9.89

- a) Cathode: Same palladium cylinder used in PDC-II experiment was used in this experiment.
- b) Cathode preparation:

To remove deuterium and tritium if any in the cathode the following method was adopted:—

- The cathode was placed in the quartz assembly connected to the high-vacuum line and slowly heated. Subsequently the electrode was heated under continuous vacuum from room temperature to 850°C. The electrode was kept at this temperature for two hours. When the electrode temperature exceeded 750°C, a black deposit was formed on the cooler parts of the quartz assembly. In view of this, heating was continued at 850°C for further two hours. No further deposit was released at this temperature. The black coating formed is being subjected to investigations to identify the nature of the deposit.
 - The electrode was brought to room temperature and the vacuum line was filled with deuterium gas at 1 cm of Hg pressure. The electrode was slowly brought to 800°C and kept for 3 hours at this temperature. After this deuterium reduction process, the deuterium gas was removed and heating was continued for additional 3 hours under continuous vacuum. After this operation the electrode was checked for any further release of gases. No further degassing was observed.
 - It may be pointed out that the black deposit initially released from the electrode turned to a silvery white deposit at this stage and this coating is under investigation.
 - The electrode after this treatment became shining silvery white and was used for this experiment.
- c) Anode: The anode was a similar platinum gauze of area 25 cm².

Cell and Accessories

The cell and accessories remained mostly similar as in PDC-II except for the following:

- Palladium catalyst of standard design was used for recombination.

- An additional recombination stage consisting of copper oxide column was used to convert oxygen depleted deuterium gas into D₂O.
- Electrochemical measurement: The details are similar as in PDC-II experiment.

Materials used in the Experiment

Heavy water: Similar grade of heavy water as was used in the previous cell was used here. The heavy water cell volume in this experiment was 80 ml.

- Electrolyte: Electrolyte was similar as in PDC-II experiment.
- The other conditions such as cooling the cell and tritium measurements were identical with PDC-II experiment.
- Sampling: The procedure followed and the volume of the samples withdrawn from the cell during the experiment remain the same.

In all during this experiment, 12 samples were taken from the start of the experiment to the end of the experiment. Other samples for tritium counting were collected from various stages of recombination from the catalyst, the water-bubbler solution and the degassed electrode.

Electrolysis

Electrolysis procedure followed was similar to PDC-II experiment. However, pulsing was introduced after 67 amp.hrs. of electrolysis at constant current mode. It may also be pointed out that the pulsing was done continuously during the day and night for the entire experiment.

- On 13.9.89 the electrolysis was reverted back to the constant current mode at 2 amp. for 3 hours, followed by pulsing till end of the experiment. The pulsing during the period was between 2 - 4 amps.
- Details of the electrolysis parameters are given in Table II.

Observations: Table IIB

- On 8.9.89 between 1300 hrs. to 1350 hrs. there was a power breakdown.
- 9 samples of the cell solution were collected from 7.9.89 to 13.9.89 for monitoring the level of tritium activity. The tritium content in the cell solution did not show an increase between 7.9.89 to 13.9.89, except that there was a marginal decrease in the samples taken on 13.9.89 compared to the samples taken on 12.9.89. In view of this, the experiment was continued with a higher pulsing parameter as that of Fleischmann experimental conditions.
- During this operation, constant current for 3 hours and pulsing for 2 hours were maintained.
- On 14.9.89 around 1000 hrs. there was a change in the cell behaviour. The bottom of the cell was shattered due to explosion. In all, the total volume of D₂O used in this experiment was 185 ml which included 105 ml of make-up D₂O and 80 ml of cell D₂O.
- Before the explosion it was noticed that the cell temperature shot up from 71°C to 80°C and the bubbling rate was low.

Observations: Table IIC

Due to the explosion at the end of the experiment all the electrolyte solution of about 80 ml was completely lost and no sample could be collected for tritium assay. Broken pieces of the cell were collected. The upper part of the cell and the broken pieces were washed and the sample was collected for counting. The D₂O condensate and the recombined water from the palladium catalyst, copper oxide and the bubbler solutions were taken for tritium counting.

The total tritium activity counted from all the samples accounted for 2,08,531 dpm while the total input tritium activity in 185 ml of D₂O used in this experiment comes out to be 30,170. It may be noted that the activity in the cell solution could not be accounted as it was lost. Even this tritium activity of 2,08,531 dpm, accounted from the recovery and recombination of gases liberated from the cell, has shown excess tritium 5.79 times.

In view of the repeated nature of the explosion at the terminal stages of electrolysis it was decided to subject the palladium cathode for a metallographic examination. Metallographic examination was done at the Physical Metallurgy Division by means of polarised light microscopy after embedding and mounting the electrode with an acrylic polymer resin. The palladium cathode was then cleaned with acetone and tetrahydrofuran to remove the polymer coating. The electrode on degassing gave about 1.2 ml of gas which accounted for 5,530 dpm of tritium activity. It may be mentioned here that if the electrode had been degassed before the metallographic examination the tritium content would have been significantly higher.

— It may be pointed out that had the cell solution not been lost, significant amount of tritium could have been recovered. An important observation from the counting of the cell samples was that large tritium activity was not produced in the cell until 13.9.89 (PDC-III-12) even at 218 amp. hrs. Excess tritium was produced only between 13.9.89 and 14.9.89. (between 218 amp.hrs and 286.2 amp.hrs.) whereas in the PDC-II experiment excess activity was generated at about 75 amp.hrs. in 3 days of electrolysis.

Results of the polarised light microscopy of the electrode

— Metallographic examination of the palladium cathode used in the experiment and which experienced an explosion showed an extensive twinning within the palladium grains with worm-like microstructure. This is suggestive of an intensive shock-wave impact on the metal. Microphotographs of the two samples are attached for reference (Figs. 1-3)

A similar palladium cylindrical cathode was also metallographically examined. This electrode was given for comparison and did not see any explosion during electrolysis. Results of metallography revealed that it did not show any significant twinning and worm-like microstructure.

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TABLE I
A. SUMMARY OF ELECTROLYSIS FOR PDC-II

		Amp.Hrs.
1	Constant current mode	10.7.89 - 12.7.89 40.33
2	a) Pulsing current mode (during day)	12.7.89 - 25.7.89 133.99
3	b) Constant current mode (during night)	12.7.89 - 25.7.89 <u>248.85</u>
		<u>423.17</u>

B. SUMMARY OF TRITIUM LEVELS IN D₂O DURING ELECTROLYSIS

Vol. Of D ₂ O/0.1 LiOD Electrolyte	= 60 ml
Tritium activity in blank D ₂ O/LiOD	= 170 dpm/ml of D ₂ O
	= $0.076 \times 10^{-3} \mu\text{Ci/ml}$ of D ₂ O

Date	Sample No.	Amp.Hrs.	Vol. of D ₂ O added ml	Tritium activity $\mu\text{Ci/ml}$ of D ₂ O	Excess tritium (times)
13.7.89	PDC-II-1	75	40	1.59	1.25×10^4
19.7.89	PDC-II-2	235.6	111	0.76	3.5×10^3
20.7.89	PDC-II-3	273.3	131	0.62	2.56×10^3
24.7.89	PDC-II-4	381.5	176	0.39	1.31×10^3
25.7.89	No sample	423.17	196	—	
26.7.89	No sample	433.32	196	—	
28.7.89	PDC-II-5	433.32	196	0.31	0.95×10^3

C. SUMMARY OF TRITIUM ACTIVITY IN THE OVERALL EXPERIMENT: PDC-II

			Tritium Activity (μCi)
INPUT: Initial volume of D_2O electrolyte	=	60 ml	
Volume of D_2O added	=	<u>196 ml</u>	
	Total		256 ml
Tritium activity in D_2O	$= 0.76 \times 10^{-3} \mu\text{Ci/ml D}_2\text{O}$ $= 170 \text{ dpm/ml D}_2\text{O}$		
Total input of Tritium activity			= 0.02

OUTPUT

Source	Vol. ml	Total activity μCi
i) End electrolysis D_2O cell-sample recovered (PDC-II-5)	52	15.96
ii) Vapour-condensate recovered	16	11.87
iii) Deoxo-recombined D_2O recovered after termination of electrolysis	16 + 52	20.82
iv) Vapour-condensate-II recovered	0.5	0.14
v) Deoxo-recombined D_2O -II recovered	2.8	0.57
vi) Bubbler (H_2O)	16	1.16
vii) Electrode gas control extracts after the electrolysis	—	0.03
viii) Samples drawn during electrolysis	8	<u>5.72</u>
		56.27

Excess tritium recovered $\frac{56.25}{0.02} = 2.812 \times 10^3$ times.

TABLE II
A. SUMMARY OF ELECTROLYSIS FOR PDC III

		Amp. Hrs
1. Constant current mode 6.9.87	9.9.89	71.75
2. Pulsing current mode	9.9.89 - 14.9.89	<u>214.87</u>
		<u>286.62</u>

B. SUMMARY OF TRITIUM LEVELS IN D₂O DURING ELECTROLYSIS

Vol. of the electrolyte D ₂ O/0.1M LiOD	= 80 ml
Tritium activity in blank D ₂ O	= 166 ± 4 dpm/ml of D ₂ O
Tritium activity in blank D ₂ O/LiOD	= 166 ± 4 dpm/ml of D ₂ O
	= 0.075 × 10 ⁻³ μCi/ml D ₂ O

Date	Sample No.	Amp.Hrs.	Vol. of D ₂ O added ml	Tritium Activity dpm/ml
7.9.89	PDC-III-4	18.0		195 ± 4
8.9.89	PDC-III-5	42.0	15	276 ± 8
8.9.89	PDC-III-6	Current stopped	—	263 ± 8
9.9.89	PDC-III-7	65.67	30	249 ± 8
10.9.89	PDC-III-8	106.12	45	216 ± 4
11.9.89	PDC-III-9	137.87	53	248 ± 10
12.9.89	PDC-III-10	170.22	65	256 ± 10
12.9.89	PDC-III-11	185.87	75	260 ± 5
13.9.89	PDC-III-12	218	80	250 ± 5
14.9.89*	no sample	286.2	105	End of experiment

* There was an explosion and entire D₂O in the cell was spilled and lost. In view of this no sample could be taken

C. SUMMARY OF TRITIUM ACTIVITY IN THE OVERALL EXPERIMENT PDC-III

INPUT:		Tritium activity (<u>dpm</u>)
Initial volume of D ₂ O	= 80 ml	
Vol. of D ₂ O added	= <u>105 ml</u>	
	Total 185 ml	
Tritium activity in D ₂ O	= 166 dpm/ml D ₂ O	
	= $0.075 \times 10^{-3} \mu\text{Ci/ml D}_2\text{O}$	
		=30,710
		(0.0138 μCi)

OUTPUT:	Source	Vol. (ml)	Total activity (dpm)
i)	Cell wash/ broken quartz pieces	2	8,592
ii)	Vapour—condensate recovered	2.5+5.0	1,14,025
iii)	Palladium catalyst recombined D ₂ O recovered	70+20	68,605
iv)	D ₂ O recovered after CuO	1+1.1	4,285
v)	Bubbler (H ₂ O)	—	3,068
vi)	Electrode gas content extracted after explosion	—	5,530
vii)	Samples drawn during electrolysis	18	4,426
viii)	End electrolysis D ₂ O cell sample*	—	—
			2,08,531
			(0.0939 μCi)

$$\text{Excess tritium recovered} = \frac{1,77,821}{30,710} = 5.79 \text{ times}$$

$$= 0.080 \mu\text{Ci}$$

* Calculation of total tritium activity does not take into account 80 ml of D₂O spilled due to the explosion.

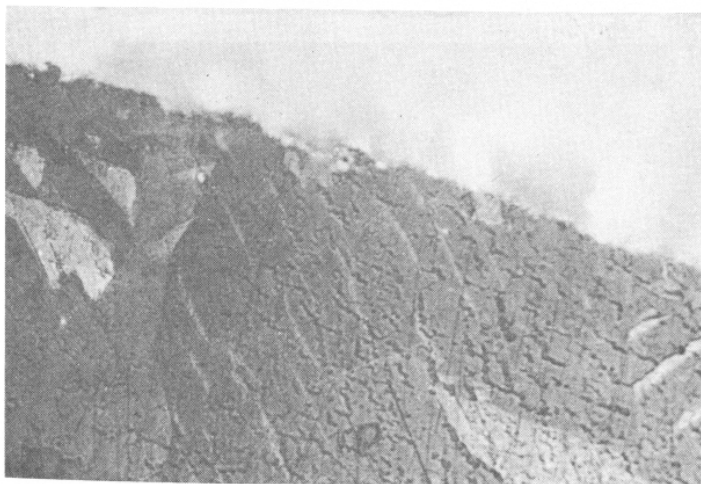


Fig. 1. Deuterium loaded Pd sample-1 after explosion.



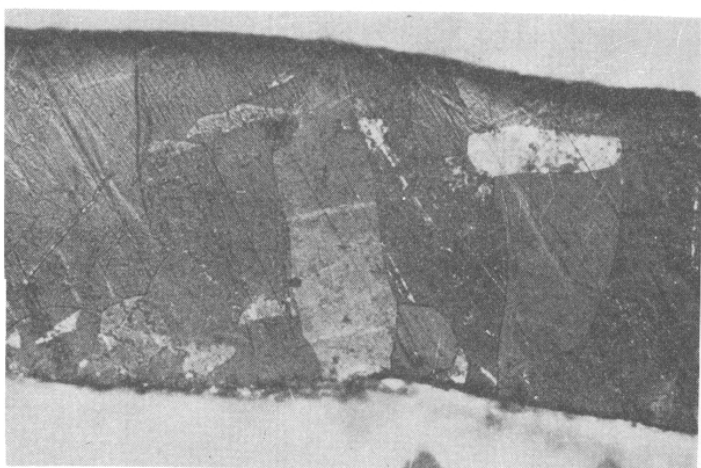
4

200x



5

125x



6

125x

Fig. 2. Deuterium loaded Pd sample-1 – another view.

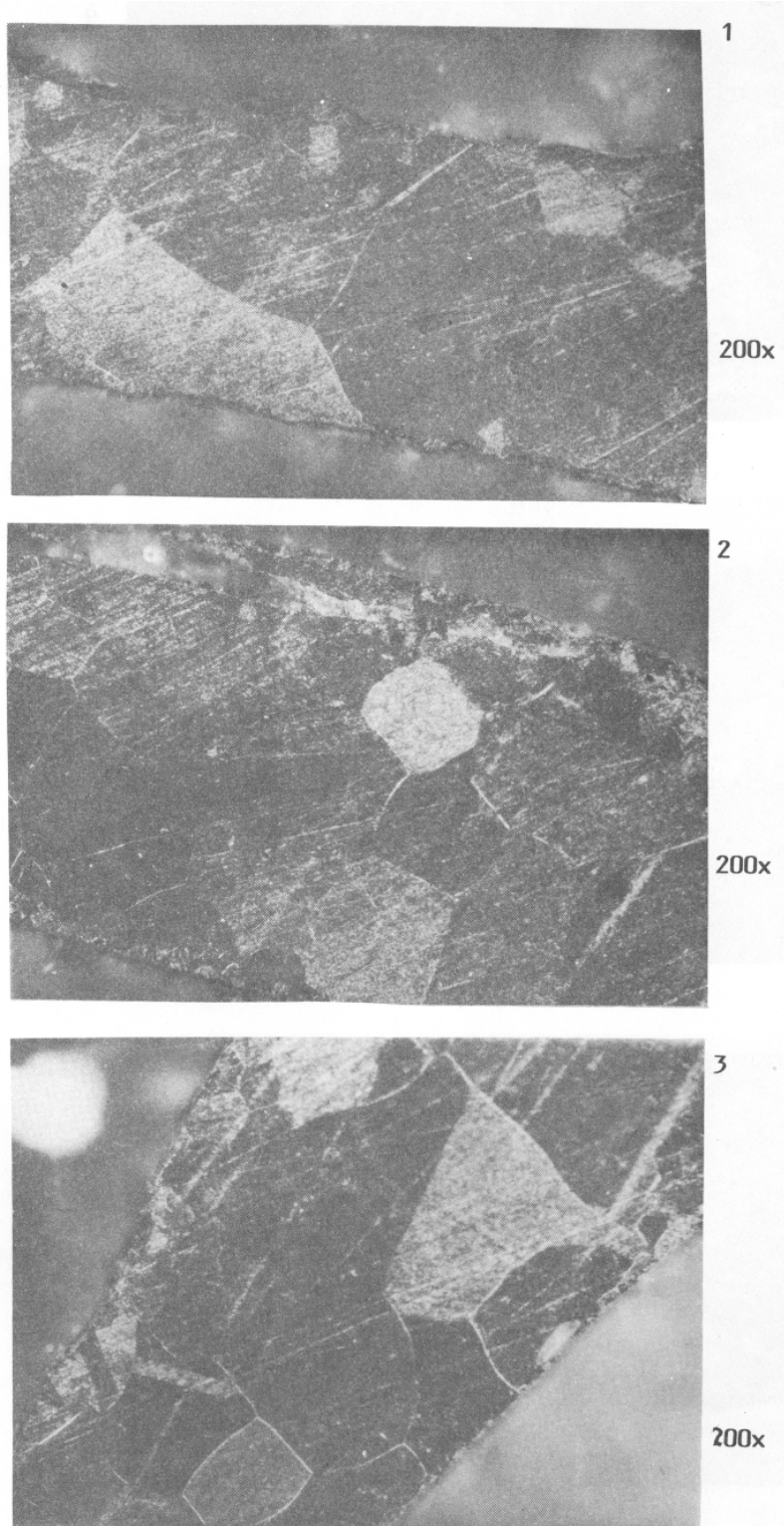


Fig. 3. Pd sample-2 annealed (550°C – 2 hours) but without deuterium loading.