

SOLID STATE AND ELECTROCHEMICAL PHENOMENA RELATED TO COLD FUSION IN TITANIUM

B. Escarpizo, F. Fernández, J. Sevilla, F. Cuevas and C. Sánchez

Dept. Física Aplicada C-IV, U.A.M., Cantoblanco, 28049 Madrid, Spain

I. Introduction

Attempts to reproduce cold fusion results/experiments follow, at least, two possible directions:

a) Improvements of characteristics (efficiency and so on) of detectors and reductions of background signals and noises.

b) Better knowledge of the system (electrolytic cell) i.e. of the cathode material and of the electrolysis itself.

We have been running several electrolytic experiments along all the past year (results will be reported elsewhere) and investigating on some electrochemical and solid state phenomena which could be related to the lack of reproducibility of cold fusion experiments. In this communication we will deal with one of them: the role played by the polycrystalline grains during the charging of Ti cathodes with Deuterium by electrolytic means.

I. Distribution of Deuterium in Titanium cathodes

It has been pointed out by several authors that a heavy deuteration of the cathode is necessary if cold fusion is to be produced. Unfortunately we have concluded that high Deuterium concentrations in the bulk of Ti cathodes are hardly obtained in current and regular electrolytic

experiments. This conclusion is, in fact, suggested in experiments by Brauer et al. (1) who determined the Hydrogen profile in Ti pieces electrolytically loaded. The profile shows a plateau of thickness $\sim 0.25 \mu\text{m}$, where Hydrogen concentration is about 62 atoms per cent (TiH_x $x \approx 2$), followed by a rapid decrease of the Hydrogen content up to thicknesses of about $0.7 \mu\text{m}$ where one finds only metallic Ti. This type of profile clearly suggests the existence of a barrier which prevents a full propagation of the Hydrogen atoms. If no barrier is present in the cathodes, and by considering that Hydrogen goes into Ti by electrolytic pressure and then diffuses into its volume, the calculated Hydrogen profile shows that Hydrogen concentration continuously decreases from a value of $x=2$ at the surface to $x=0$ at a thickness as large as $4 \mu\text{m}$, seven times larger than the one found in the real experiment.

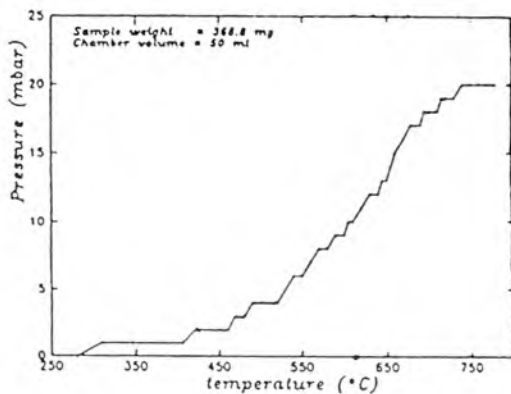


Fig.1. Accumulated pressure versus heating temperature during thermal desorption of Deuterium from one of the Ti cathodes used in electrolytic cold fusion experiments.

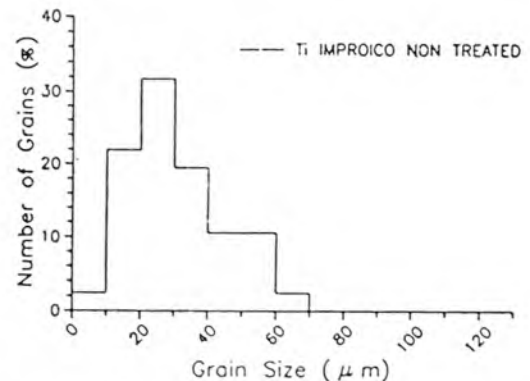


Fig.2. Distribution of grain size in commercial Ti plates. Number of grains is plotted against its size.

We have tested this point of view with all the Ti cathodes used through about twenty electrolytic cold fusion experiments. By using Thermal Desorption (TD) of the absorbed Deuterium and by applying Differential Scanning Calorimetry (DSC) to the same cathodes, we have concluded (2) that full deuteration of the cathodes is only produced in a layer close to the surface of thickness between $5\text{--}10 \mu\text{m}$. Results of Thermal Desorption of one

of our samples are shown in Fig.1, where the Deuterium accumulated pressure is plotted against the sample temperature during its heating up to $\sim 800^{\circ}\text{C}$ where the Hydrogen pressure reaches a plateau. Same results have been obtained with all the others samples used in our electrolytic experiments.

The electrolyte was in ten experiments acid and in three of them basic and the electrolysis charge in Ah ranged from about 290 Ah to 2080 Ah. All the results confirm that deuteration of our Ti cathodes takes place in a layer of thickness between 5-20 μm with Deuterium concentrations ranging between $x=1$ and $x=2$. Some authors apply X-ray diffraction to confirm that they have produced TiD_2 . But this is a misleading tool because it gives only information on the structure of a layer equal to the penetration of the X-rays. In fact, some of our cathodes have been examined by XRD and Deuterium concentrations between $x=1.5$ to $x=1.8$ have been obtained, in agreement with the former conclusion because the penetration depth of the $\text{CuK}\alpha$ X-ray line is smaller than $\sim 10 \mu\text{m}$.

III. Role played by polycrystalline grains

By using Optical and Electron Microscope Microphotographs we have determined the grain size of the different Ti cathodes used in our experiments before doing electrolysis. Results are shown in Fig.2 where the number of grains (in %) is shown against its size in μm . Although there is a grain size distribution between $\sim 5 \mu\text{m}$ and $\sim 70 \mu\text{m}$, the peak of the distribution is for all the plates in grain sizes of 20-30 μm . This predominant grain size corresponds quite well to the thickness of the deuterated layer of the cathode we have found by other techniques. We therefore may draw the following picture of the deuteration process of commercial Ti used as cathode in electrolytic cold fusion experiments. Deuterium diffusion is limited by the grain boundaries of the polycrystalline pieces which act as barriers for the Deuterium propagation. Therefore, the first layer of grains appears with high Deuterium concentration, often close to $x=2$, and the rest of the cathode with practically no Deuterium.

The proposed deuteration process of Ti has been further confirmed in the case of Ti cathodes electrolyzed in basic electrolytes. Microphotographs from the SEM show the existence of wide cracks between grains after prolonged electrolysis. These cracks appear as a consequence of the



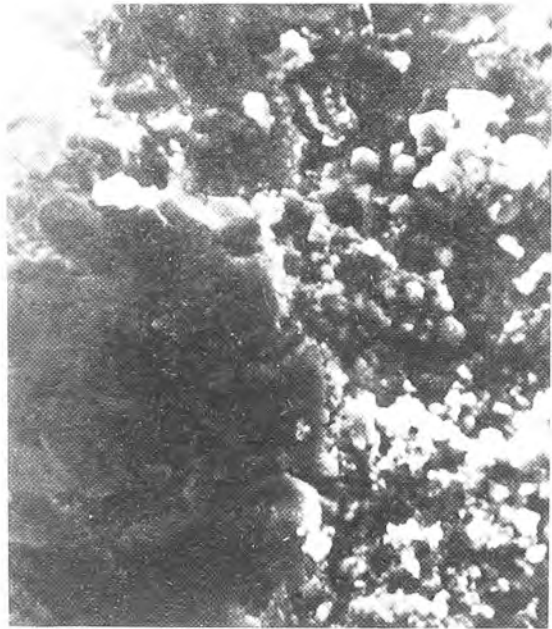
a)

120 μm



b)

12 μm



c)

8.6 μm



d)

10 μm

Fig.3. Scanning Electron Microscope photographs of: a) Surface of a Ti where elevations due to grain dilatations can be seen. b) A crack appearing on the top of "mountains" like the one in a) is shown. c) Surface of a Ti cathode where part of the grains have already dropped. d) Facets of clean Ti grains appearing after the first layer of deuterated grains released from the cathode.

dilatation of the grains induced by Deuterium absorption. Grains press one against each other forming elevations like mountains (photo a) of Fig.3) and on the crests of those mountains, where the grain boundary is, a crack appears (photo b)). Once the cracks are large enough, the grain releases from the cathode and drops to the bottom of the cell. This is shown in photograph c) where some grains have been already released. Finally, when a high enough number of grains have dropped from the cathode, a new and clean surface of it has to be deuterated, as can be seen in photograph d), where the facets of clean grains of the Ti cathode are visible. A qualitative picture of this mechanism is shown in Fig.4. This mechanism seems to be no operative in cathodes deuterated in acid electrolytes. At least, the morphology of the cathode surface after the experiments is very different. It resembles a spongy surface with many cavities and a large effective area.

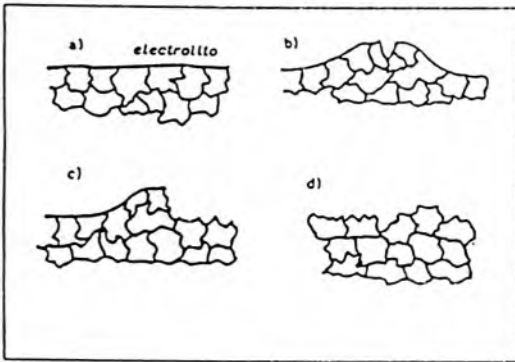


Fig.4. A qualitative picture of in the deuteration mechanism of a polycrystalline Ti cathode.

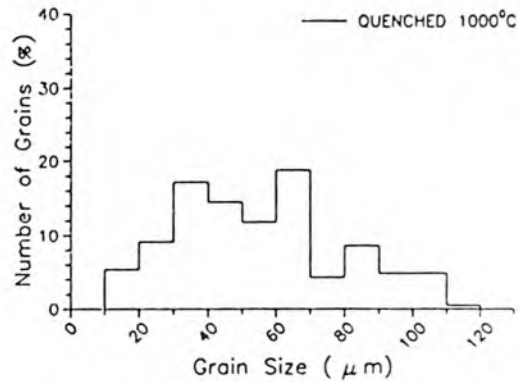


Fig.5. Distribution of grain size in quenched commercial Ti (to be compared with Fig.2).

The reason why the grain boundaries act as a barrier for Deuterium diffusion seems to be the gettering effect of Oxygen, Nitrogen, etc. atoms adsorbed there. Many authors anneal their samples in vacuum before the experiment in order to eliminate the gases adsorbed on the surface of the boundaries. However, the success of this pretreatment is not guaranteed at least a mass spectrometer be connected to the annealing camera to measure the desorbed gases.

We are trying in our experiments another approach to increase the deuterated volume of our Ti cathodes: to enlarge the grains by a thermal quenching. Some results are shown in Fig.5. Some samples quenched in water from different furnace temperatures show grain size distributions whose

peak increases with the furnace temperature. In fact, samples quenched from 10^3 °C are formed by grains with volumes 30 times larger than those of the untreated samples what means that the deuterated volume will be 3 times larger. In these cases and, if the surface cathode has been conveniently cleaned, the grains must be fully deuterated in a matter of hours with conventional current densities.

IV. Conclusions

We therefore can conclude from the content of this communication that:

Deuteration of Ti cathodes in electrolytic cold fusion experiments seems to take place in only the first grain layer. Grain boundaries seem to be barriers for the propagation of Deuterium in the next grain layer.

Differences in behavior are found between the hydrides formed in acid and basic electrolytes. In basic media, used by most of the authors, the deuterated grains release from the cathode and a new and clean surface of Ti appears periodically.

V. References

- (1) E. Brauer, R. Gruner and F. Rauch, Ber. Bunsenges. Phys. Chem., 87, 341-345, (1983)
- (2) J. Sevilla, B. Escarpizo, F. J. Fernandez and C. Sanchez, Fus. Tech., 19, 188, (1991)