Bernardini, M., et al. *Anomalous Effects Induced by D2O Electrolysis of Titanium*. in *8th International Conference on Cold Fusion.* 2000. Lerici (La Spezia), Italy: Italian Physical Society, Bologna, Italy.

ANOMALOUS EFFECTS INDUCED BY D_2O ELECTROLYSIS OF TITANIUM

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1 Summary

This investigation emphasizes the heat output (~1 W) measured at open circuit after the electrolysis of 0.6 M K_2CO_3 in D_2O on titanium. This thermal phenomenon decayed slowly over the course of several days. "Post-mortem" γ-spectroscopy analysis of the Ti samples cathodized in D_2O evidenced transient γ-emissions which cannot be attributed to impurities of the electrolytic system.

2 Introduction

Since Fleischmann and Pons announced they had induced D-D fusion into a Pd lattice by electrolytic deuterium loading [1], it was speculated that the phenomenon might not be restricted to Pd only. Titanium soon appeared a viable alternative to Pd. Thus, the Frascati ENEA group first [2] and others later [3-5], after submitting the Ti – D_2 system to thermal cycles, were able to detect sporadic neutron emissions of energy compatible with D-D fusion. That the Ti lattice could constitute a suitable host for low energy nuclear reactions of hydrogen isotopes is also stressed by recent reports on D^+ implantation onto TiD_2 targets [6-8], whereby unpredicted fusion channels would operate in the solid and thereby greatly enhance the fusion rates.

But what about the induction of nuclear phenomena at Ti by D_2O electrolysis? To address this question, much careful work has been performed by Sanchez and his group [9-10] but without definitive results, due probably to the difficulty of the Ti-water system.

Water discharge at a Ti cathode can lead to Ti hydride formation in acid media [11], where evolving hydrogen directly interacts with the bare metal. Indeed, several reports qualitatively account for Ti hydride formation from acidic electrolytes, whereas hydriding seems hindered at pH ≥ 9 [12]. However, the extent and penetration of the electrolytic reaction are expected to be very low, as indeed confirmed by Escarpizo *et al* [10].

The efficiency of electrolytic hydriding could therefore be increased by operating at temperatures near boiling, but not in acid electrolytes owing to the possible dissolution of Ti at open circuit. Here we have chosen to perform the electrolytic experiments at temperatures near boiling (95° C) by using a relatively mild alkaline electrolyte (0.6 M K_2CO_3 in D_2O, pD=11.3), wherein the metal is stabilized by surface oxides.

3 Experimental Procedures and Results

3.1 Electrochemical tests

Ti foils (purity ≥ 99.5%, 0.02-0.07cm thick) were supplied by Goodfellow, Johnson Matthey and a local producer. The typical Ti sample working electrode was a square with area of 1.5cm^2; the counter electrode was a Pt coil; the reference was Ag|AgCl KC1 sat. The Ti sample was charged galvanostatically at I = -200mA for periods ≥ 24 h, either at 25° C or at 95° C, while a continuous flow of N_2 removed the electrolysis gas from the cell.

At electrolysis interruption, we observed the relaxation with time of the open circuit electrode potential and accordingly divided the various Ti samples into three groups: two groups that gave totally different responses and one group that gave intermediate response.

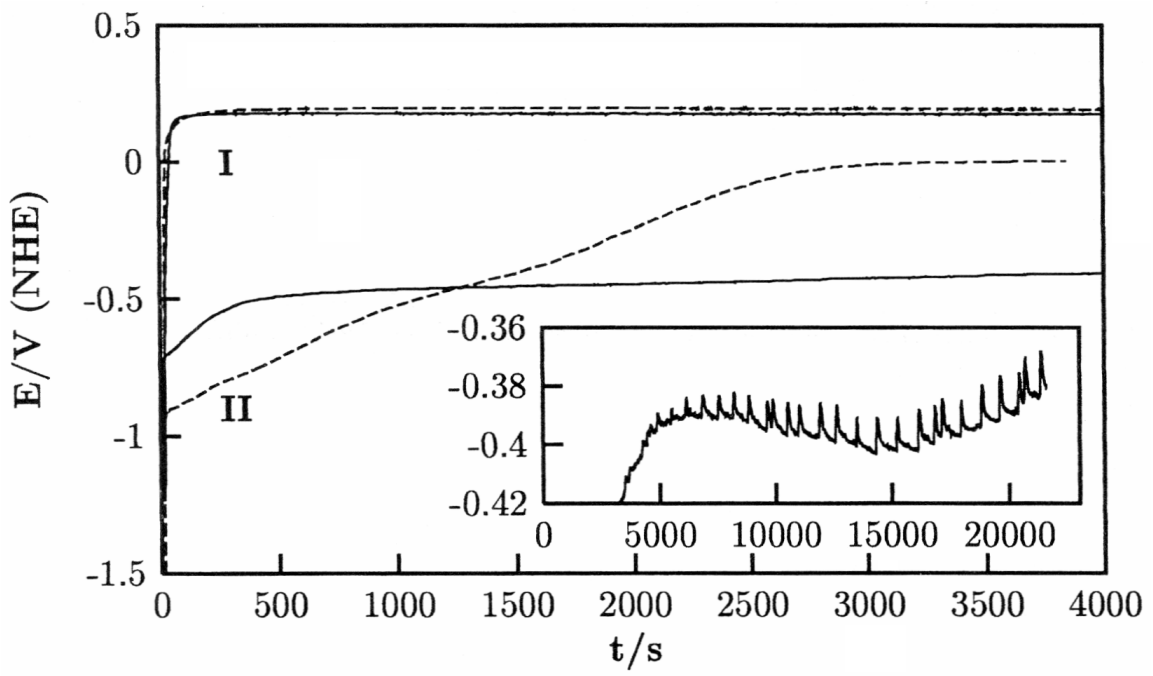

Figure 1: Ti electrode potential transients following the electrolysis interruption

Figure 1 illustrates the two limit behaviours at 25° C (broken curves) and 95° C (plain curves) of two samples I and II. For sample I at both temperatures, electrolysis interruption was followed by a fast potential increase to attain the potential of TiU2 [11].

For sample II, at 25° C the potential of TiO_2 was eventually achieved after a slowly increasing potential transient, whereas at 95° C the rate of potential increase dropped with fluctuations and oscillations, as the insert of Figure 1 shows. We associate the behaviour of Sample II with the decomposition (by corrosion) of a bulk hydride phase, the formation of which had occurred much more efficiently at 95° C than at 25° C.

3.2 Calorimetry

The calorimetric runs were carried out at 95° C [13-14]. The core of the calorimetric system was a Dewar electrolytic cell equipped with a refrigerated column to condense the vapour. In addition to the (Ti) cathode and (Ni) anode, the cell was further equipped with a Pt 100 thermometer, a NiCr resistance heater and a glass pipe conveying a controlled N_2 flow ($3.5cm^3\ min^{-1}$) into the electrolyte to ensure homogeneous heat distribution.

The cell, filled with 100ml of 0.6 M K_2CO3 in D_2O and immersed in a silicon oil bath kept at 95 ±0.01° C by a Hake F3 thermostat, was made isothermal with the bath by supplying continuously the power required for NiCr resistance. In the experiment detailed below we have chosen to measure the free temperature increments (above 95° C) and convert them into power through repeated calibrations (typical cell constant was $2.0\pm0.1°CW^{-1}$).

Figure 2(a-d) accounts for the evolution with time of the calorimetric response during electrolysis at a Ti cathode from the same batch of sample II (1.2 cm χ 2.5 cm χ 0.07cm). The left ordinate gives, with accuracy ±0.1° C, the increment in temperature of the electrolyte (continuous line). The right ordinate gives, with accuracy ±0.1 W, the power correspondingly determined by the cell constant. The accuracy of this datum is lower than that of the thermometric readings since we considered the range 95-97° C, ΔT/° C linear with P/W. The two broken lines indicate (E-1.52 V) × I (*i.e.*, electrolytic joule power-------) and E × I (*i.e.*, total electrolysis power — · —) fed to the cell.

Note therefore that as soon as the electrolysis was initiated (Fig 2a) firstly with I = -75mA, the electrolyte temperature quickly increased well above the provisions of the Joule effect to then exhibit a smooth decline. This latter trend was reversed by applied -250 mA (Figure 2b) and a temperature jump occurred at electrolysis interruption.

Figure 2a

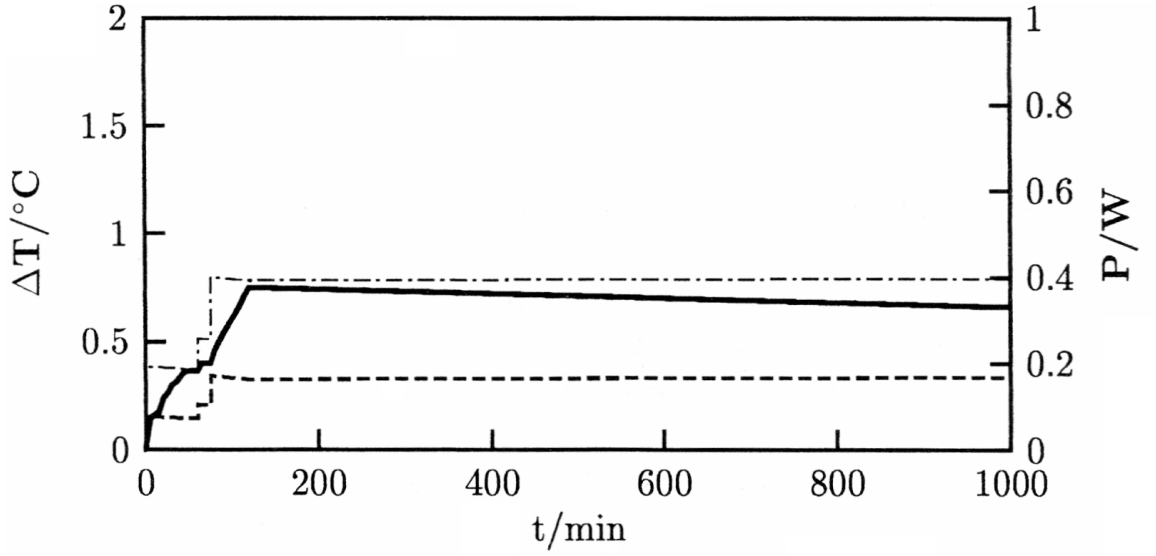

Figure 2b

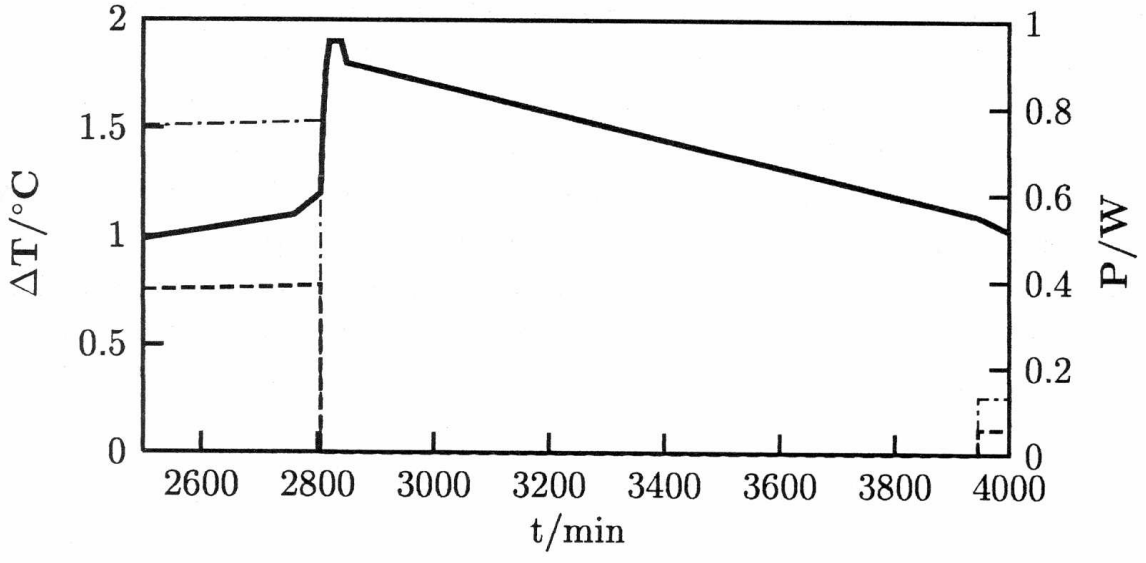

Figure 2c

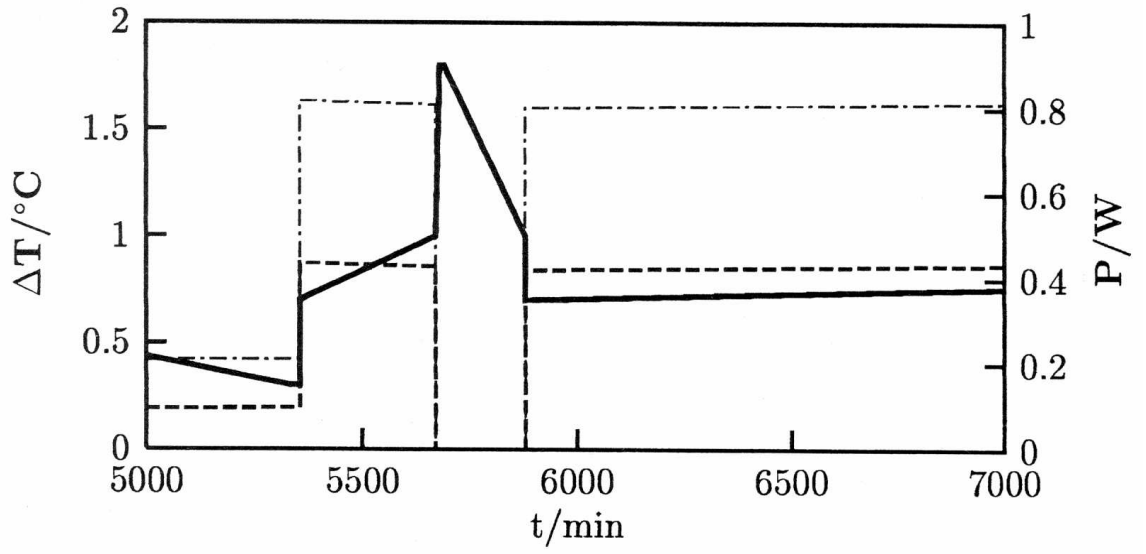

Figure 2d

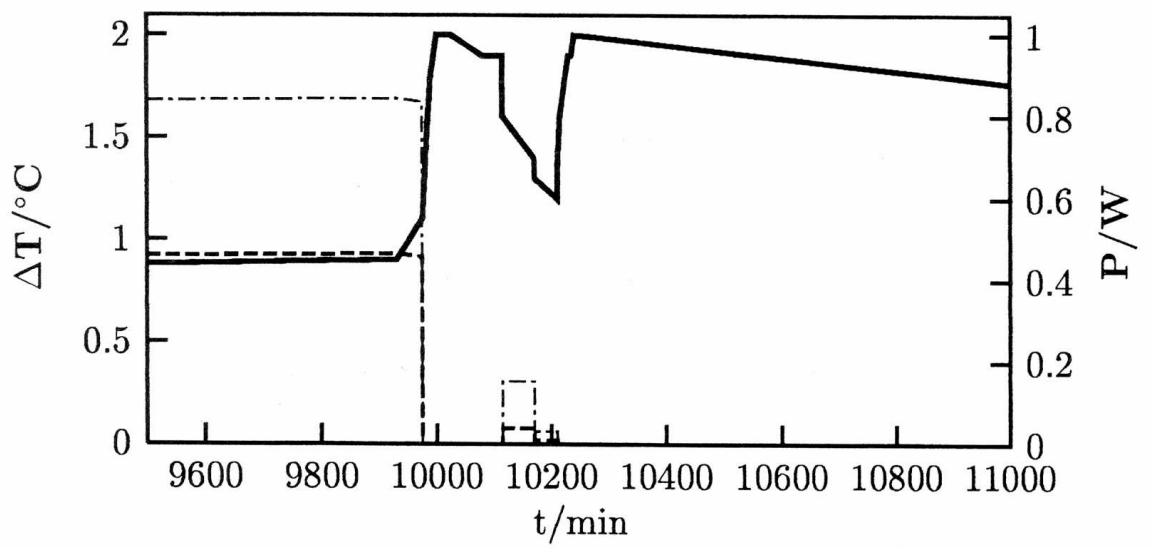

Figure 2: Evolution with time of the calorimetric response.

The relaxation time of the thermal phenomenon (days) clearly had nothing to do with the Dewar cell heat loss characteristics. Upon applying I = -50/-75mA for ~24h, the temperature steadily declined as if the thermal phenomenon had been totally quenched (Figure 2c). With I = -250mA the electrolyte temperature rose, and later, at a new electrolysis interruption, the thermal effect then relaxed much more quickly than before. At this stage, -250mA were applied for another 3 days (Figure 2d) and when the electrolysis was stopped, the thermal output at open circuit appeared remarkably steady (although it could easily be quenched by applying even -15mA as Figure 2d shows). Since then, the spontaneous relaxation of electrolyte temperature required several days, whereby some hundred Kj supply from an unknown source can be inferred.

3.3 γ-Spectroscopy equipment and procedure

To establish whether the anomalous heat release could have involved other anomalous effects such as nuclear transmutations to meta-stable nuclides, some Ti samples (of typical dimensions 4.5cm × 1.5cm × 0.02cm) submitted to D_2O (H_2O) electrolytic discharge, were then ("post mortem") examined by γ-spectroscopy, by using two high-resolution Ge γ detectors working in coincidence (Fig 3).

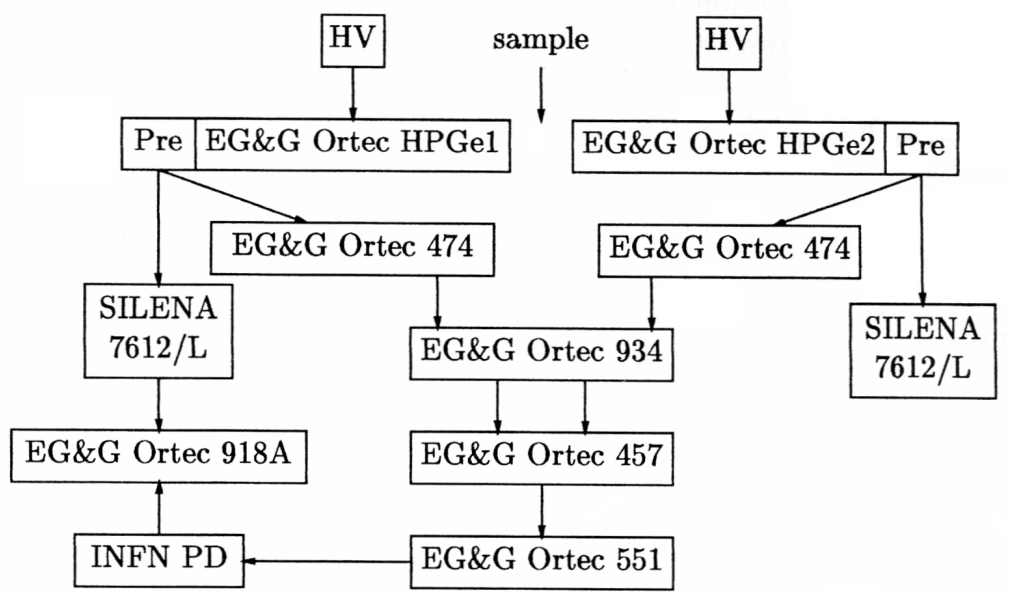

Figure 3: Scheme of the gamma-gamma coincidence system utilizing two Ge detectors.

The linear signals from the amplifiers were first shaped to the best energy resolution (time constant = 6 μs), then amplified and finally sent to the multi-channel analyser for spectral analysis. The analyser accepted the detected signals only when they were above a threshold energy value (~ 800 keV) and in coincidence within a pre-fixed resolution time (< 500ns).

The former condition was controlled by the constant fraction discriminators. The second condition was verified by the time-amplitude converter. The signal from this converter was synchronized with the linear signal entering the analyser in coincidence mode. Energy calibration of Ge detectors was systematically performed both before and after the spectroscopic experiments, by using six lines of the natural background (^{208}Pb,^{228} Th,^{214} Po). In the γ measurements, the maximum deviation was in the range 0.14 - 0.19 keV, whereas the error due to electronics could have reached 0.27- 0.38 keV.

4 γ-Spectroscopy Results

A Ti sample, cathodized some weeks in light water, was examined as a preliminary experiment; this constituted the blank for the other experiments.

As γ-cascade source, we have considered the hypothetical occurrence of the nuclear reation

$$^{47}\text{Ti} + \text{H} \rightarrow [\text{intermediate state}] \rightarrow {}^{48}\text{V} + 6830\ \text{keV} \qquad (1)$$

whereby β^+/EC unstable ^{48}V originates ^{48}Ti*, which then decays to the ground ^{48}Ti state with the two γ photon emissions [15].

After monitoring this sample for over one week, 45 d after the end of the electrolysis, no peak was detected. For the Ti sample cathodized in heavy water, we hypothesized the nuclear reactions producing γ cascades to be:

$$^{48}\text{Ti} + \text{D} \rightarrow [\text{intermediate state}] \rightarrow {}^{46}\text{Sc} + {}^{4}\text{He} + 3891\ \text{keV} \qquad (2)$$

$$^{50}Ti + D \rightarrow [\text{intermediate state}] \rightarrow {}^{48}Sc + {}^{4}He + 3686\ keV \quad (3)$$

The half-life of ^{46}Sc (reaction 2) is 83.81 d and the γ cascade to ^{46}Ti ground state is constituted by two photons of energy equal to 889.277 and 1120.545 keV respectively [15]. The half-life of ^{48}Sc (reaction 3) is 43.7h and γ cascade to ^{48}Ti consists of γ photons of energy equal to 983.524 keV, 1037.522 keV and 1312.050keV respectively [15].

In Experiment A, we examined a Ti sample cathodized for 20 d, which eventually showed 0.2-0.3W heat output at open circuit. The sample was placed in the γ spectrometer 8 d after the end of the electrolysis, whereby only the occurrence of reaction (2) was investigated.

Table 1: γ-Spectroscopy Results

Experiment		Length (s)	Energy (keV)		Counts
			Expected	Measured	
A	Run 1	934000	889.277	890.26±0.34	21±7
			1120.545	1122.91±0.35	22±5
	Run 2	647000	889.277	889.55±0.31	4±8
			1120.545	1121.17±0.36	7±6
B		163000	983.254	982.85±1.24	8±5
			1037.522	1036.44±0.32	17±4
			1312.099	1308 ~ 1316	4±4

The measurement consisted of two spectra acquisition runs lasting 11 d (run 1) and 8 d (run 2), with a 70 d interruption between each run. The data reported in Table I were obtained by a MAESTRO II search program which automatically identified peak energy and area. Compared to the blank, the peak area in run 1 resulted from 3 to 4 standard deviations, whereas in run 2 the said peaks decreased to ~1 standard deviation.

In Experiment B, a Ti sample, again cathodized in D_2O for 20 d (excess heat production of ~ 0.2 W), was introduced into the γ-spectrometer (~ 2 h later) and monitored for 46 h.

Two of the three expected lines (983 and 1037 keV) were found and metered by the automatic research system (cf. Table I), while the 1312 line was estimated by us, with reference to the backgrounds. The intensity of the automatically detected lines ranged from 4.2 to 1.6 σ and was seen to fade by the end of the measurement.

From the data of Table I, corrected for γ-spectrometer efficiency, the radioactivity of either ^{46}Sc or ^{48}Sc was extrapolated to a hypothetical steady state between production and decay to obtain the respective values of $6.5(\pm1.8) \times 10^{-2}s^{-1}$ and $3.2(\pm0.9) \times 10^{-2}s^{-1}$.

Acknowledgments

The authors wish to thank C. Baiocchi and Profs. F. Gramigna, F. Brandolini, M. Nigro of INFN-Legnaro for making possible our γ-spectroscopy investigation. Thanks are also due to Torresin s.r.l for the Ti supply and to the INFN group of Trieste for the loan of a data acquisition system.

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