

Deuterium Concentration Profiles and Crystallization Anomalies in Electrolytically Deuterated Titanium Plates

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ABSTRACT

Deuterium concentration and distribution profiles in electrolytically deuterated Ti plates have been obtained by Elastic Recoil Detection (E.R.D.), Rutherford Back Scattering (R.B.S.) and X-ray diffraction (XRD). It has been found that D/Ti ratio remains constant (≈ 1.65) up to a penetration which depends on the electrolysis time and then it goes down steeply to ≈ 0.05 . The formed deuteride (TiD_x , $x \approx 1.65$) exhibits some preferred orientations and its texture depends on that of the original Ti plate. The relevance of these data in relation to electrolytic cold fusion experiments is discussed.

1. Introduction

It has been emphasized by different authors that cold fusion phenomena may only be expected whenever high deuterium concentrations (stoichiometric ratio or even higher) be reached in the deuterated metal. Many papers have dealt with this problem in deuterated Pd cathodes but not enough attention has been paid to other metals like Ti and only a few papers have discussed the real atomic ratios (D/Ti) that can be obtained by electrolytic loading. On the other hand, a second condition that seems to be needed to observe cold fusion phenomena is that non equilibrium conditions (produced by any internal or external agent) must exist in the deuterated metal. In this context the knowledge of the real structure and texture of the formed deuterides and of their inhomogeneities becomes relevant. In this paper we dealt with both problems: deuterium concentration profiles in electrolytically formed TiD_x are presented and discussed. Some anomalies in the TiD_x crystallization have also been observed and correlated with the texture of the original Ti plates.

2. Experimental

Electrolytic Ti plates ($\approx 15 \cdot 15 \cdot 1$ mm) were polished and etched. After thoroughly cleaning with D₂O they were used as cathodes in an electrolytic cell with two Pt plates as anodes. After loading for ~ 1000 h with current densities of about 500 mA/cm^2 the Ti cathodes were again cleaned and cut in several pieces ($\approx 5 \cdot 5 \cdot 1$ mm) to be used in different analysis. After these steps, it was observed that Ti pieces presented a slight deformation as shown in Fig 1. No attempt was made to correct the plate curvature.

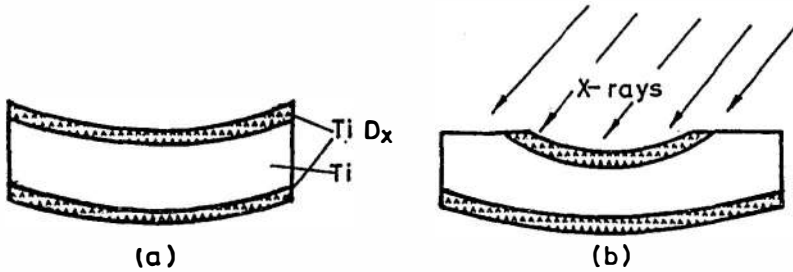


Figure 1. Deuterated Ti pieces (ETi24) as used for ERD and XRD measurements.

Deuterium concentration profiles in two Ti cathodes (ETi20 and ETi24) have been obtained by ERD and RBS techniques (experimental set up shown in Fig 2). The penetration depth of the α -particles (1.6 Mev) is around $0.5 \mu\text{m}$ with spot size $\approx 1 \text{ mm}^2$. In order to get quantitative deuterium concentrations the cross section of the elastic ${}^4\text{He}({}^2\text{H}, {}^2\text{H}){}^4\text{He}$ reaction must be known. Besenbacher et al. calculated this cross section from 0.8 to 2.3 Mev and recoil angles from 0° to 35° with a $\pm 5\%$ uncertainty. The most important problem in our

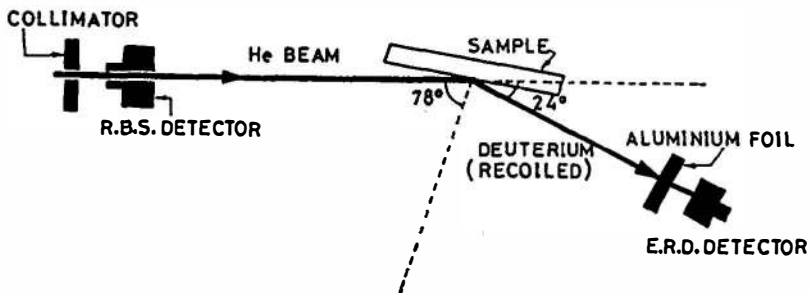


Figure 2. Experimental set-up used in ERD and RBS experiments (LNETH, Lisbon, Portugal).

measurements was the maximum Ti depth accessible to the ^4He ions. To overcome this difficulty a layer of the formed deuteride was removed after each ERD measurement by polishing (0.25 μm diamond powder) the sample.

In the same deuterated Ti-cathodes X-ray diffraction patterns were obtained and results from ETi24 are now presented. A Philips machine mod. PW1140 was used. Penetration depth of the Cu $K\alpha$ line was $\approx 5 \mu\text{m}$. The X-ray spot covered fully the investigated plate.

3. Results

It was detected that a deposit was formed during electrolysis at the cathode surface. Analysis (both by ERD and XRD) of this surface layer showed that it was composed by nickel oxide, magnesium oxide and small traces of Pt. Some details on the characteristics of this layer were reported at the Como Conference (B. Escarpizo et al 1991): This surface deposit was removed by polishing before accomplishing ERD and XRD measurements.

Typical results from ERD-RBS measurements together with the RUMP fit are shown in Fig.3 and 4. It is apparent that the near surface fit of the spectrum is not as good as that of the flat zone. Deuterium concentrations were obtained from the spectrum flat zone. Results obtained after removing several layers are shown in Fig 5 up to a penetration of 200 μm for both ETi20 and ETi24. Although it is difficult to know the depth scale error it has been estimated to be $< 10\%$ after micrometric measurements before the first and after the last polishing.

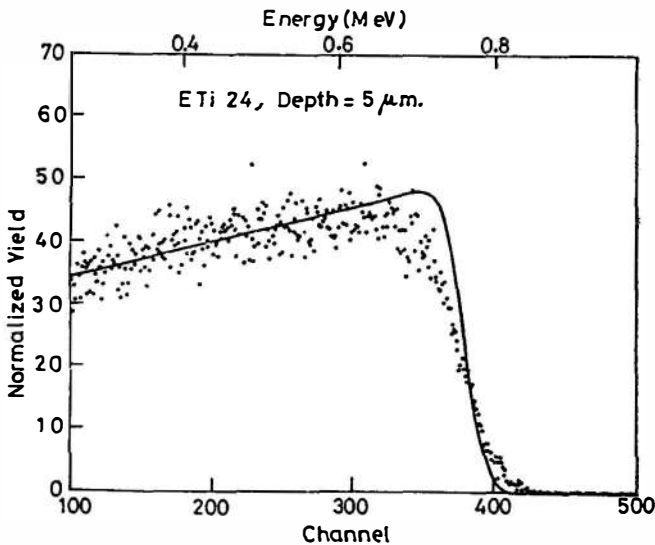


Figure 3. ERD spectrum and RUMP fit from ETi24.

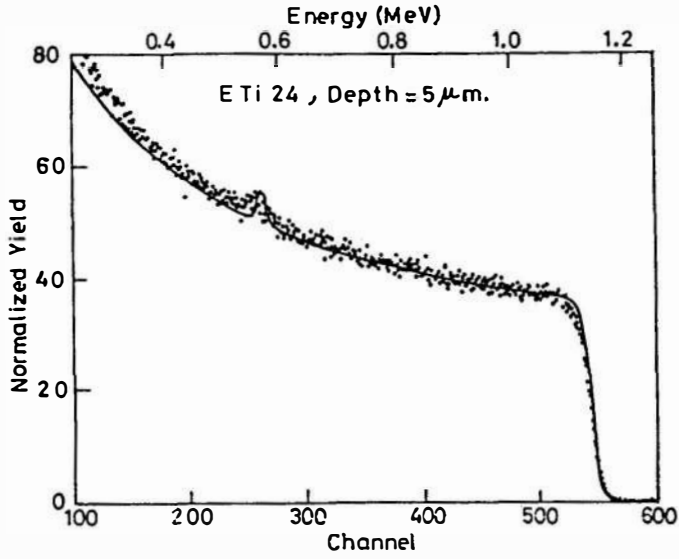


Figure 4. RBS spectrum obtained in parallel with the ERD data of Fig.3.

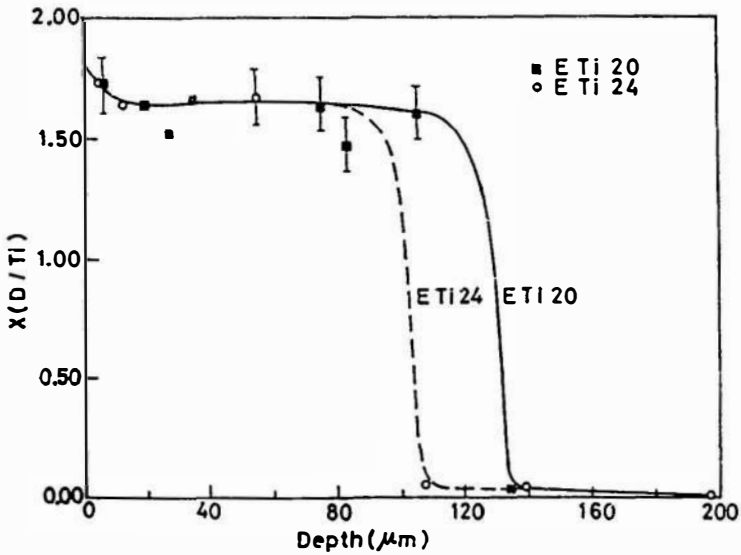


Figure 5. Deuterium concentration profiles in ETi20 and ETi2 cathodes as obtained from ERD data.

Both samples show a similar behaviour: an initial zone ($\leq 10 \mu\text{m}$) where D concentration is not clearly defined followed by an extended region, up to $120 \mu\text{m}$, where D/Ti remains constant an equal to ≈ 1.65 . After that a step decrease of D/Ti takes place within a thickness of around $20 \mu\text{m}$. This region is more clearly seen in ETi20 than in ETi24 due to the experimental points of Fig.5. Finally a very low atomic ratio (from 0.05 to 0.005) is measured up to penetrations of $\approx 200 \mu\text{m}$ (more clearly seen in ETi24 sample).

Fig.6 shows evolution of some peak intensities with depth from XRD patterns obtained with ETi24. Maximum D penetration depth is confirmed by spectra of Fig.6 as far as the intensities of all detected TiD_x peaks go down to zero at a depth of 110-120 μm in ETi24. Fig.6a shows the evolution of (220) peak of TiD_x. In Fig.6b intensities of the (311) TiD_x and (103) Ti peaks are plotted. The first one corresponds to $d = 1.342 \text{ \AA}$ and the second one to $d = 1.332 \text{ \AA}$, and only a peak appeared in the pattern at the same 2θ ; so we have concluded that the intensity of this peak should be the summed intensities of both (311) TiD_x and (103) Ti peaks. Finally in Fig.6c the intensity of (222) TiD_x peak is shown. Several other peak intensities from the XRD patterns could have been selected to be plotted but the three ones in Fig.6 make a full representation of the whole.

4. Discussion

First important result we must emphasized is that D penetration depth in our samples is confirmed by both types of measurements, ERD-RBS and XRD. In the experimental conditions used in the electrolytic loading a maximum D penetration of 110-120 μm is produced. But we must say that different D penetration depths into Ti will be produced if the electrolysis experimental conditions (time and current density) are changed. This conclusion is confirmed by results from different authors (Brauer et al. 1983, Briand et al. 1990, Sevilla et al. 1991). Brauer et al. used electrolysis times ranging from 5 to 100 s. and current densities from 5 to 200 mA/cm^2 . They obtained H concentration profiles of the same shape as those shown in Fig.5 and maximum H/Ti ratios of the order of 1.65, very close to those from ETi20 (1.60) and ETi24(1.68). Penetration depths $< 1 \mu\text{m}$ were recorded in their experiments. On the other hand, Briand et al. concluded that D penetration is 2-3 μm and that TiD₂ is formed. They used an electrolysis time of 1-3 h. and 8 mA currents. Sevilla et al. proposed that D penetration should be of the order of 20 μm . As can be seen from Fig.5 of this paper the existence of a thin layer close to the surface region with D/Ti > 1.6 can not be disregarded. So we can conclude that at best higher D concentrations (close to D/Ti ≈ 2) would be produced in a surface layer ($\leq 1 \mu\text{m}$) of the deuterated Ti plate. In the rest of the piece a limiting (D/Ti) concentration of ≈ 1.6 -1.7 seems to exist although we must say that other authors (Millenbach et al. 1982, Dus et al. 1992) have reached different conclusions on this point. Millenbach et al. formed TiD_x ($x=1.78$) samples with 20 mA/cm^2 , but the H concentrations were determined by

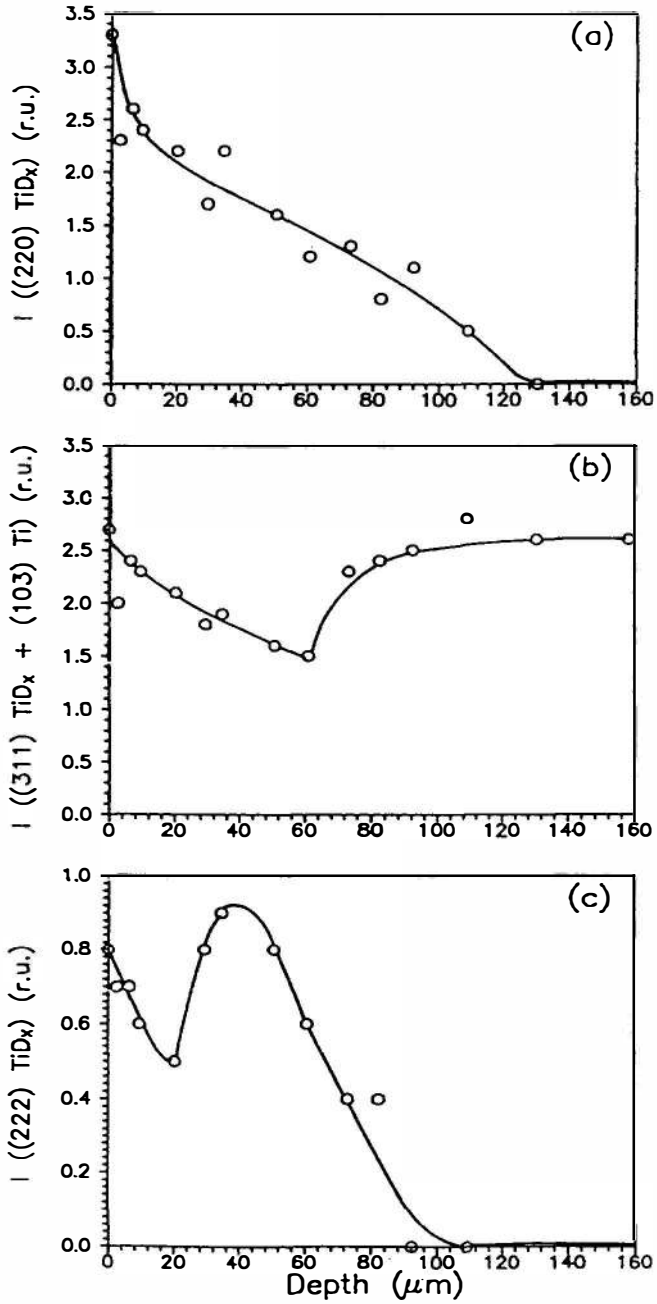


Figure 6. XRD peak intensities versus penetration depth in TiD_x formed in ETi24. (a) $\rightarrow(200)$ peak. (b) $\rightarrow(311)$ TiD_x and (103) Ti peaks. (c) $\rightarrow(222)$ TiD_x peak.

comparing lattice parameter measurements with those from calibrated samples. This method is not a direct one and accuracy of the measurements could be questionable. Dus et al. prepared Ti thin films (300 Å) and studied H absorption from gas phase at temperatures between 78°K and 298°K. They found that the maximum H/Ti is temperature dependent and $x=2$ was obtained at R.T. Probably these results are not incongruent with our data as far as layers close to the surface of the electrolytically deuterated pieces are taken into account.

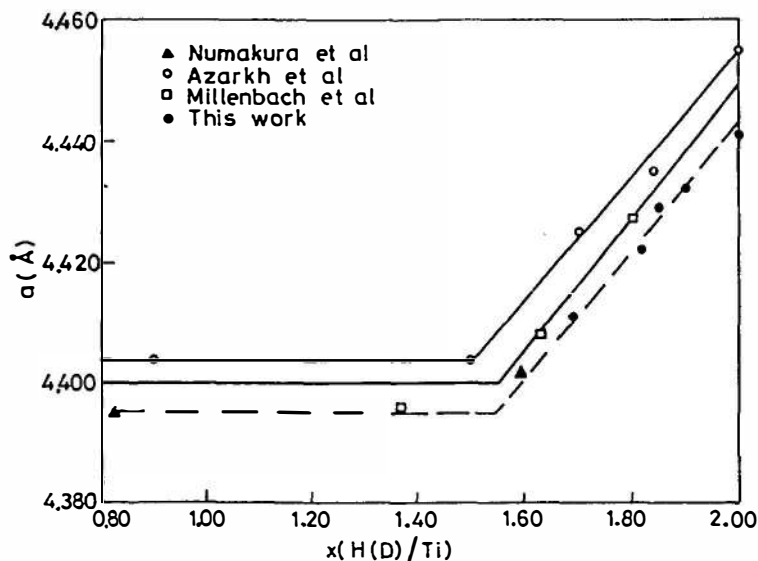


Figure 7. Variation of lattice parameter with atomic ratio, H(D)/Ti, in the H-Ti system.

From the above considerations a limit in the D concentration in electrochemically loaded Ti is a real possibility. Energetic reasons may explain these concentration limit. The change in the TiD_x (TiH_x) lattice parameter as a function of H(D)/Ti and the phase diagram of the H-Ti system are shown in Fig.7 and 8. The boundary between phases α and δ seems to establish the limit of the H/Ti ratio at room temperature.

Finally, anomalies in the crystallization of TiD_x (Fig.6) are well explained by examining the texture of the Ti plate before being deuterated (Fig.9). Due to the production process some preferred orientations are also observed. We must emphasize that the (002) Ti and (222) TiD_x peaks correspond to planes of highest packing in the hexagonal and cubic lattices of Ti and TiD_x respectively.

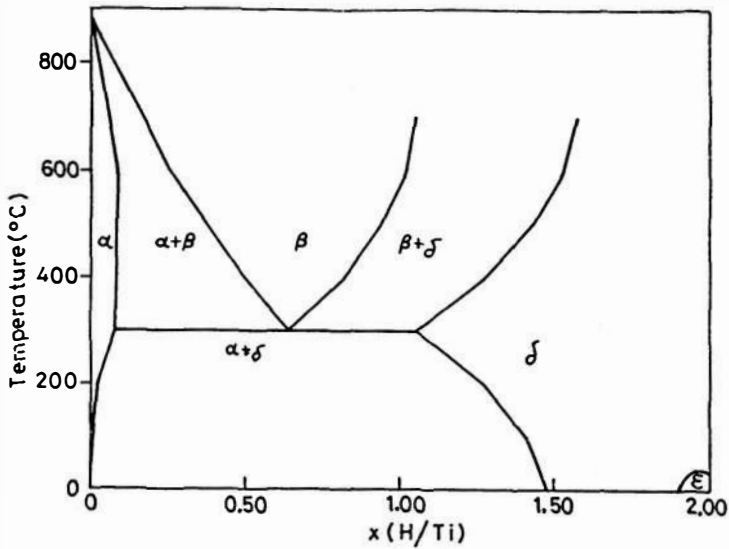


Figure 8. Phase diagram of the H-Ti system.

5. Conclusions

From this papers the following conclusions can be drawn.

- a) Nuclear results from several cold fusion experiments in Ti (Jones et al. 1989, Sanchez et al.. 1989) should be corrected in relation to the fusion reaction rates when given per cubic centimeter of the deuterated cathode material.
- b) More investigations have to be done to find the experimental way of improving the D/Ti ratio in electrolytic loading.
- c) Every piece of metal to be used as cathode in a cold fusion experiment has to be previously investigated. Anomalies in texture (and other properties) might be well related to the non equilibrium conditions required to trigger cold fusion reactions.

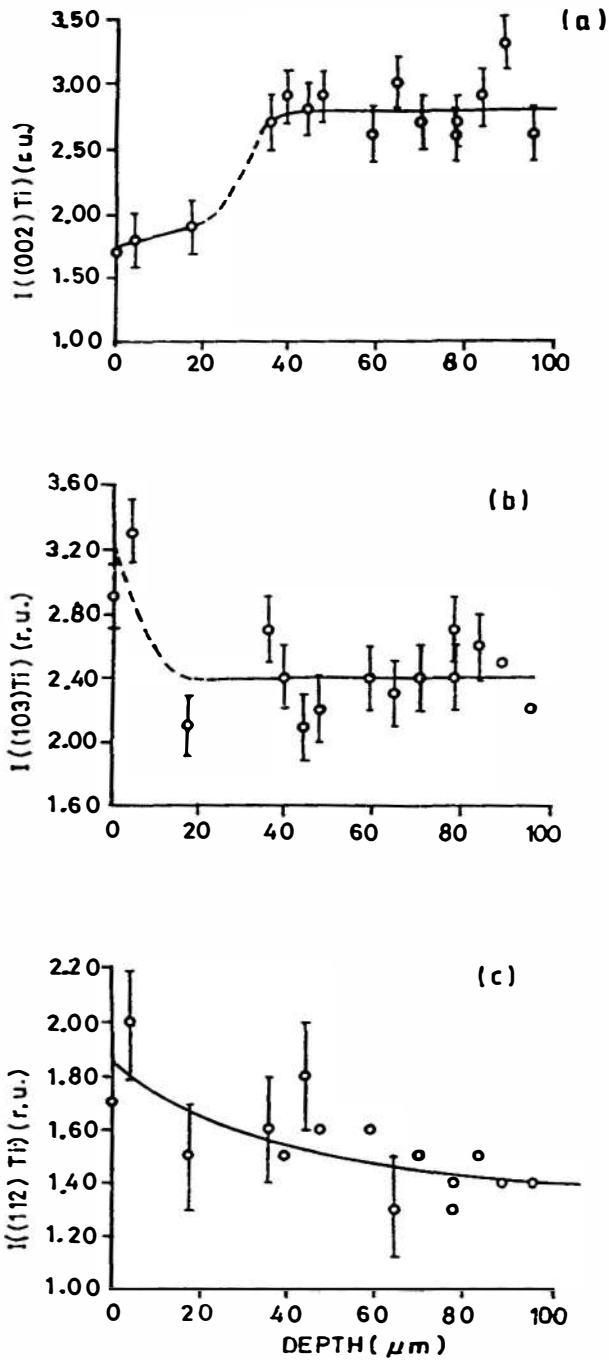


Figure 9. XRD peak intensities versus penetration depth from a Ti plate similar to ETi24. (a) \rightarrow (002) peak, (b) \rightarrow (103) peak, (c) \rightarrow (112) peak.

6. References

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