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EXCESS HEAT AND UNEXPECTED ELEMENTS FROM ELECTROLYSIS OF HEAVY WATER WITH TITANIUM CATHODES

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ABSTRACT

Excess heat was produced at the rate of about 1.2 watts during electrolysis of heavy water with a titanium cathode weighing 0.0625 g. Analysis of the electrodes before and after electrolysis with a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS) revealed that new surface topographical features with concentrations of unexpected elements (S, K, Ca, V, Cr, Fe, Ni, and Zn) formed during electrolysis.

INTRODUCTION

Previously, we reported on our findings of excess heat and unexpected elements from electrolysis with palladium cathodes and an electrolyte containing either D₂O and H₂SO₄ or H₂O and H₂SO₄ [1]. We now present results of similar experiments using titanium cathodes and an electrolyte containing D₂O and H₂SO₄.

EXPERIMENTAL METHODS AND RESULTS

Pure titanium foil (0.25 mm thick, 99.99 + % Ti) was spot-welded to platinum lead wire and made the cathode in an electrolytic cell with a platinum anode and 15 ml of electrolyte containing 0.01 mol fraction H₂SO₄ (reagent) and 0.99 mol fraction D₂O (99.9 atom % D). Recombination catalyst (platinized Al₂O₃) was suspended above the electrolyte, and the cell was sealed. An identical cell containing a platinum cathode was connected in series. This cell was used as a control to measure heat effects by comparison with the titanium-cathode cell. An automated data acquisition system monitored cell voltages, six thermocouples attached to each cell (Fig. 1), and the ambient temperature. Constant current was used during the experiments.

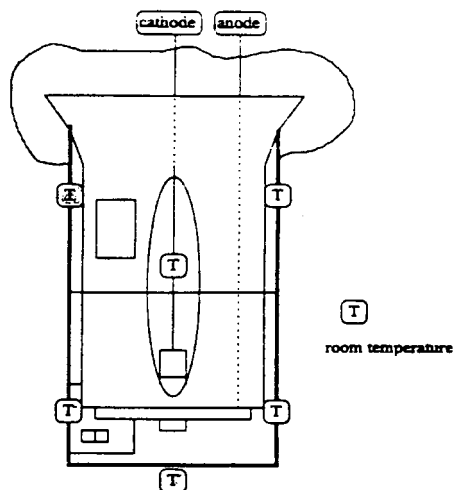


Fig. 1. Placement of thermocouples on the outsides of the control and experimental cells.

Using constant current of 0.55 A resulted in a current density of about 2 A per square cm on the titanium cathode. This current was passed for about 33.5 hours. The resulting power input and temperature-time data for each cell are shown in Fig. 2. It should be noted that the control (C) cell was taken out of the circuit after about 23 hours due to excessive loss of electrolyte.

Fig. 2a shows that the temperature of the titanium (D) cell exceeded that of the platinum control (C) cell. Fig. 2b shows that the power input to the C cell clearly exceeded the power

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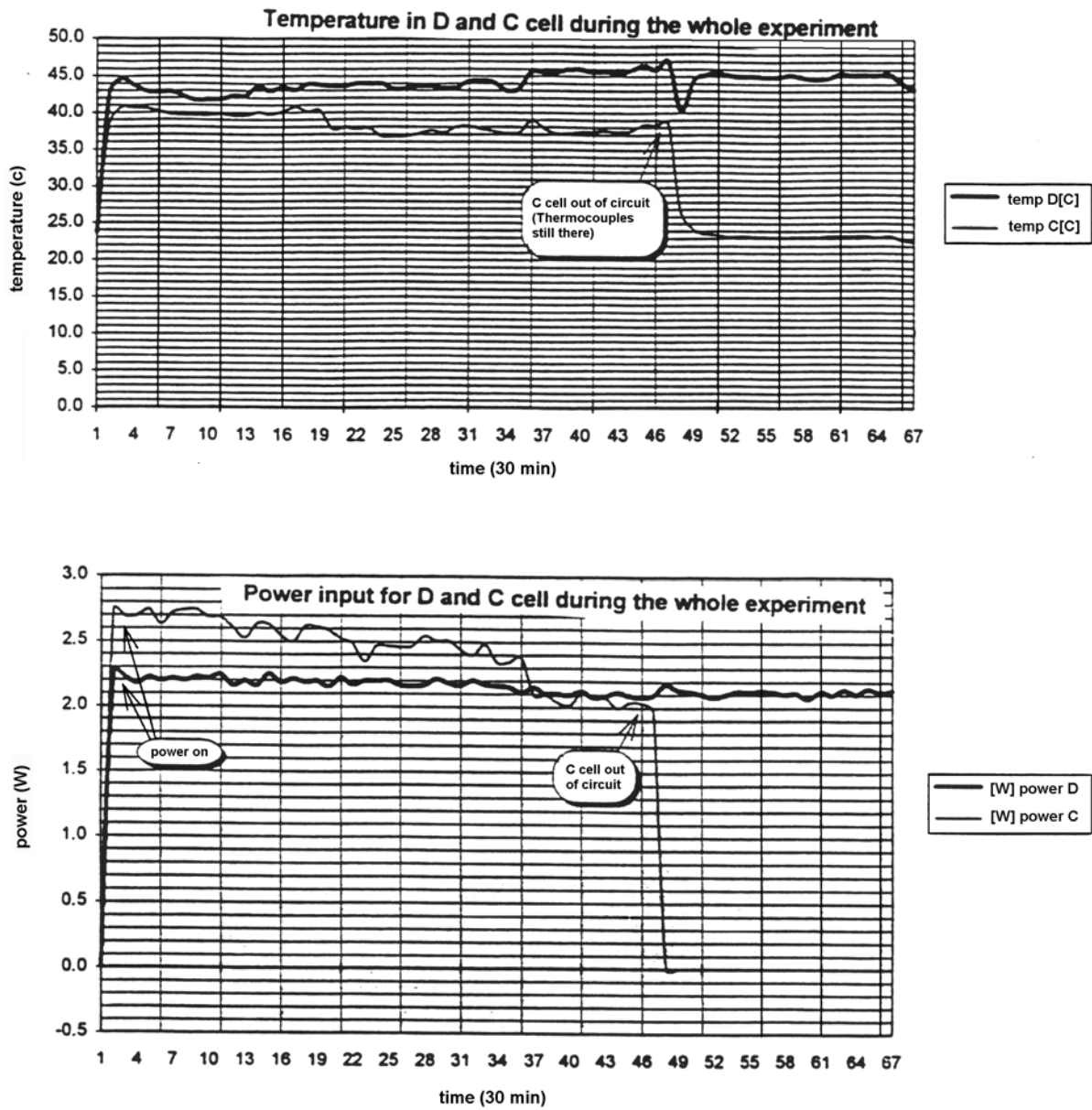


Fig. 2. (a) Temperature and (b) power versus time for the platinum-cathode control (C) and titanium-cathode (D) cells.

input to the D cell during the first 18 hours. Excess heat may have been produced by the D cell. This can be calculated by considering the power input, the heat produced by the combination of titanium with hydrogen isotopes, losses due to escape of gases through the tops of the cells, and the heat loss to the surroundings due to the thermal gradient between the cells and the surroundings.

The following equations give the rate of enthalpy change in each cell:

$$\text{C (control) cell: } dH(C)/dt = IV(C) - dH(C_{esc})/dt - R) T(C)$$

$$\text{D cell: } dH(D)/dt = IV(D) + dH(TiD)/dt + dH(XS)/dt - dH(D_{esc})/dt - R) T(D),$$

where $H(C)$ and $H(D)$ are each the enthalpy of the C and D cells, respectively, $H(TiD)$ is the enthalpy released by formation of TiD , $H(C_{esc})$ and $H(D_{esc})$ are each the enthalpy which escapes from its respective cell due to incomplete recombination, $H(XS)$ is the excess enthalpy produced in the D cell, I is the constant current which

passed through both cells, $V(C)$ and $V(D)$ are the cell voltages, R is the rate of heat loss by each cell to the surroundings, and $\Delta T(C)$ and $\Delta T(D)$ are the temperature differences between each cell and ambient.

At steady state, which was reached in about 45 minutes, the enthalpy gain equals the enthalpy loss for each cell, so each equation can be set equal to zero. The enthalpy lost due to escape of gases is determined from the weight lost by each cell. For the C cell, this was 285 calories for the whole experiment (23 hours for the C cell), which gives $dH(C_{esc})/dt$ equal to 0.0034 calories per second. The average power input to the C cell during one hour at steady state $IV(C)$, was 0.644 calories per second. Then the first equation is solved for R , using $\Delta T(C)$ of 16.5 C. This gives R equal to 0.0388 calories per degree C. This is used in the second equation.

About 40 calories is produced by conversion of the entire titanium cathode to TiD , so $dH(TiD)/dt$ is about 0.0003 calories per second. $IV(D)$ is 0.525 calories per second, $dH(D_{esc})/dt$ is 0.0012 calories per second, and $\Delta T(D)$ is 20.6 degrees C. Solving for $dH(XS)/dt$ gives 0.28 calories per second, or 1.15 watt.

Geiger-Mueller counters were used to monitor radiation from the C and D cells throughout the experiment, and LiF chips sealed in plastic were in each cell during the experiment. The counters showed slightly higher amounts of radiation coming from the D cell, but the standard deviation was too high to have confidence in this data. The LiF chips showed no significant difference from background.

The titanium cathode was examined before and after electrolysis with SEM and EDS. Before each examination, the electrode was cleaned ultrasonically several times, each time for 5 minutes with deionized water. Fig. 3 shows that there are many changes in the surface topography. Those regions labeled a through h in Fig. 3b were examined in detail at higher magnification. A typical result is shown in Fig. 4, which is an enlargement of area e in Fig. 3b. This shows that cracking occurred along the edge of the sample. The protrusion labeled (a) gave the EDS spectrum in Fig. 5a, and point (b) gave the EDS spectrum in Fig. 5b. The protrusion shows the presence of many elements of both higher and lower atomic number than titanium. The concentrations of these elements is far higher than can be expected from the composition of the original material. In contrast to this, Fig. 5b shows that point b in Fig. 4 is almost pure titanium. Spectra similar to Fig. 5a were found in the other areas indicated in Fig. 3b.

In another, similar experiment, the current density during electrolysis was about 0.5A per sq. cm instead of 2A per sq. cm. The excess heat was about 0.5 watt for a titanium electrode from the same lot, of about the same mass. This electrode was also examined before and after electrolysis with SEM and EDS. The comparison of images is given in Fig. 6.

The double-headed arrow in Fig. 6b shows a feature which was not present on the titanium cathode before electrolysis. A portion of this feature is shown enlarged in Fig. 7. The bright spots (a) and (b) were used for the EDS spectra in Fig. 8.

DISCUSSION OF RESULTS

The results obtained with thin foil titanium cathodes are similar to those we obtained with thin foil palladium cathodes, using $H_2SO_4 - D_2O$ electrolyte [1], in that excess heat and unexpected elements are obtained reproducibly in both cases. A significant difference is that excess heat is observed from the very beginning of electrolysis when a titanium cathode is used, whereas there is an incubation time when a palladium cathode is used. The duration of the incubation period depends on the thickness of the Pd foil. At 0.025 mm it is about one hour, and at 0.1 mm it is about one day. The magnitude of the excess heat seems greater for titanium than for palladium under equivalent conditions.

The EDS spectra in Fig. 5a and Fig. 8a indicate the presence of chromium and vanadium. It is likely that both of these spectra contain both Cr and V because of the overlap of V Kbeta with Cr Kalpha. The chemical analysis provided by the supplier gave 0.910 ppm V and 1.150 ppm Cr, whereas Fig. 5a and Fig. 8a show concentrations of these elements more than four orders of magnitude higher. The feature which gave the spectrum in Fig. 5a may have been an inclusion which extruded above the surface due to swelling caused by hydride formation. **But the spectrum in Fig. 8a came from a surface eruption, similar to those where silver was observed on palladium [1].** Evidence of time-dependent changes in the silver spectrum which could indicate the changing of silver to cadmium was also presented [2].

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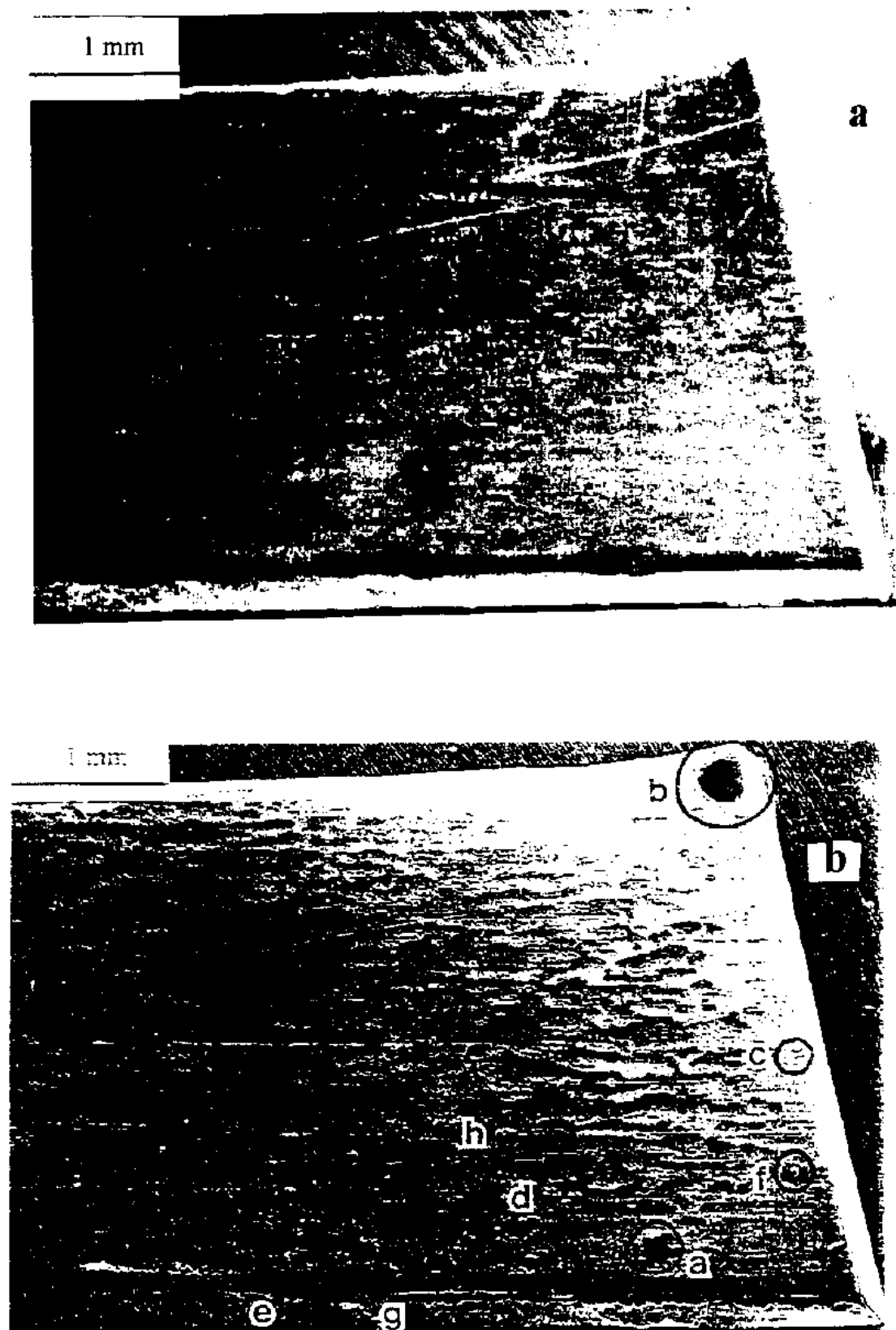


Fig. 3. Titanium cathode before (a) and after (b) electrolysis.

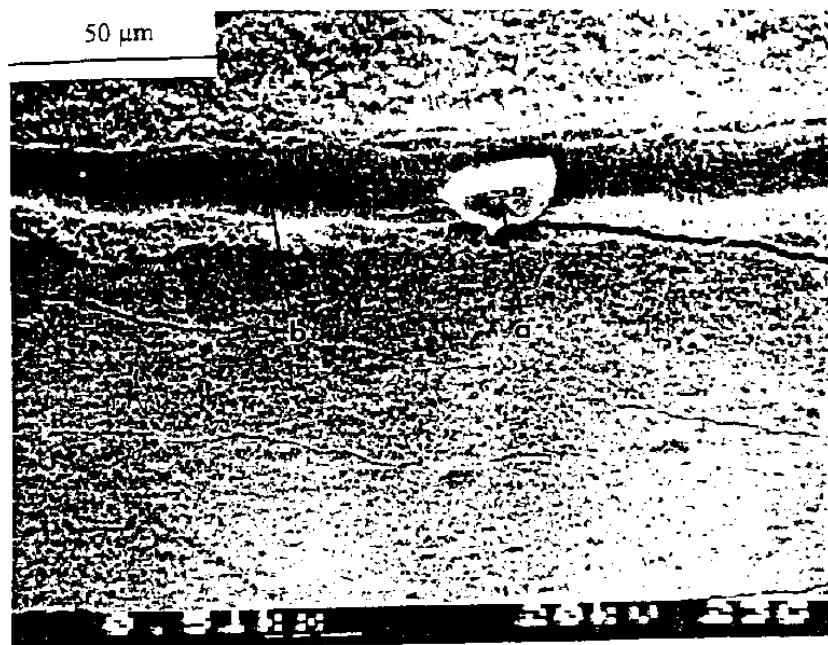


Fig. 4. Enlargement of region (e) in Fig. 3.

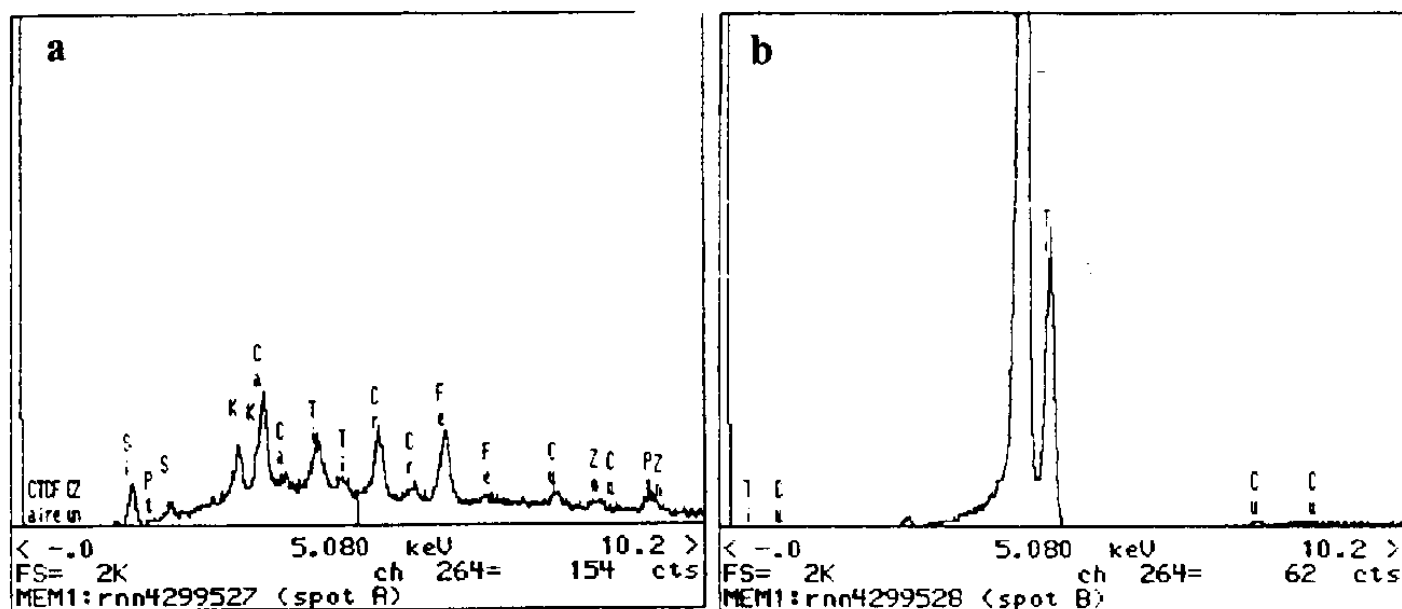


Fig. 5.(a) EDS spectrum from spot (a) in Fig. 4, and (b) EDS spectrum from spot (b) in Fig. 4.

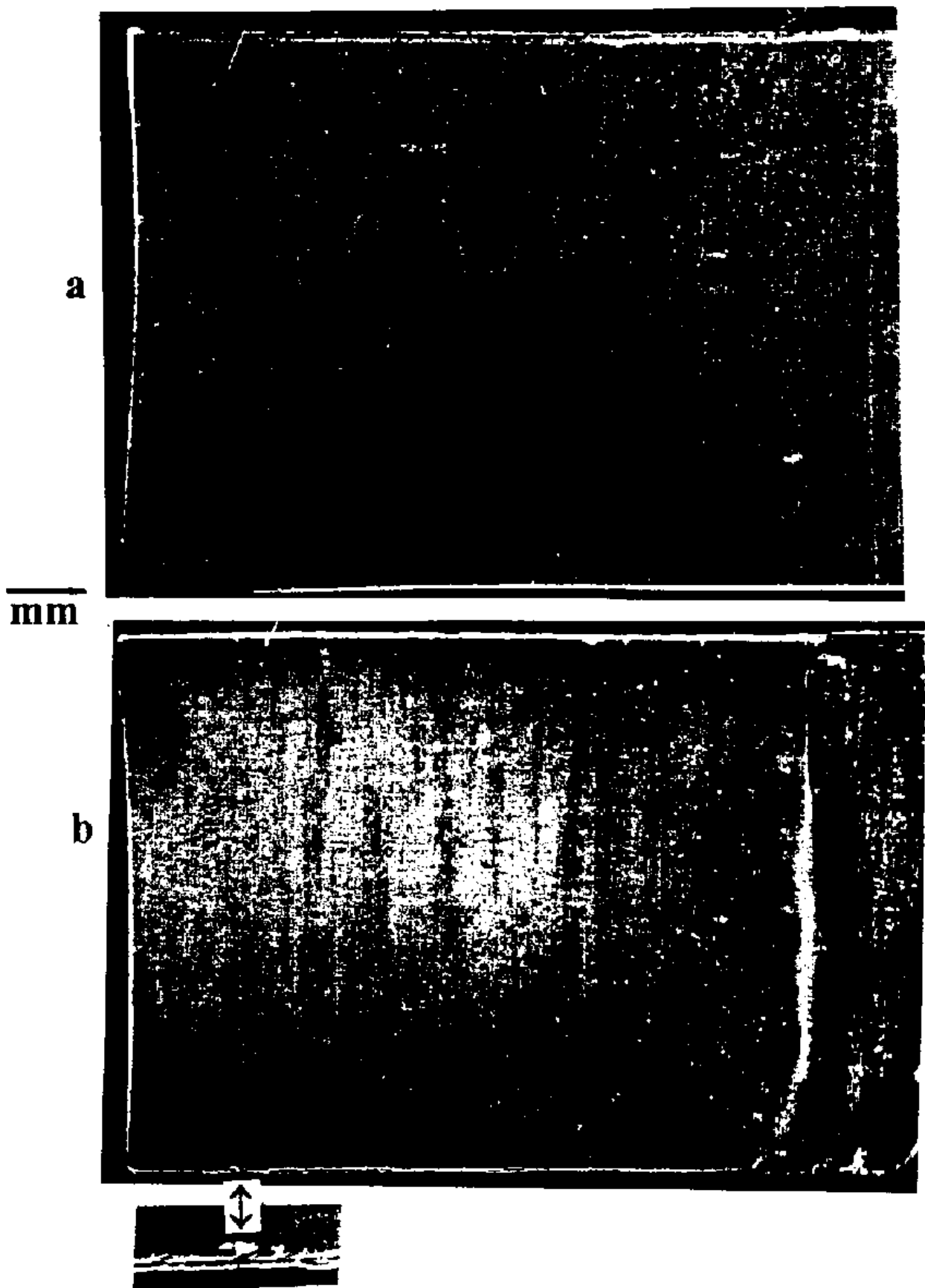


Fig. 6. Titanium cathode (a) before and (b) after electrolysis, using 0.5 A/sqcm. The arrow shows a new feature and its enlargement.

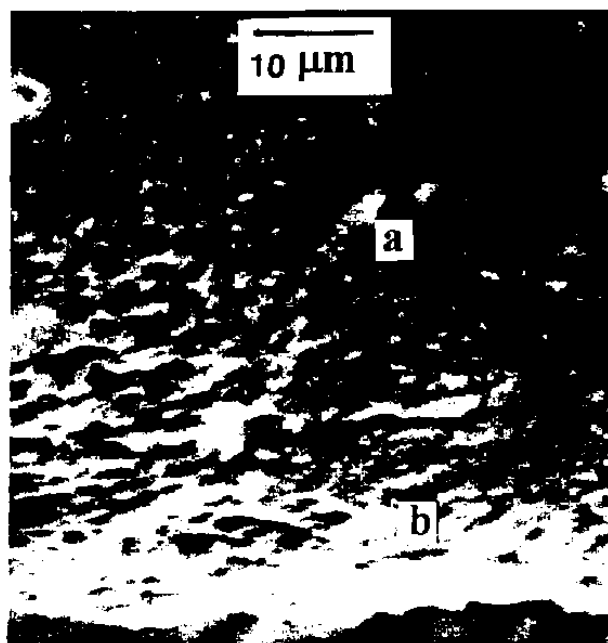


Fig. 7. Enlargement of the new feature shown in Fig. 6.

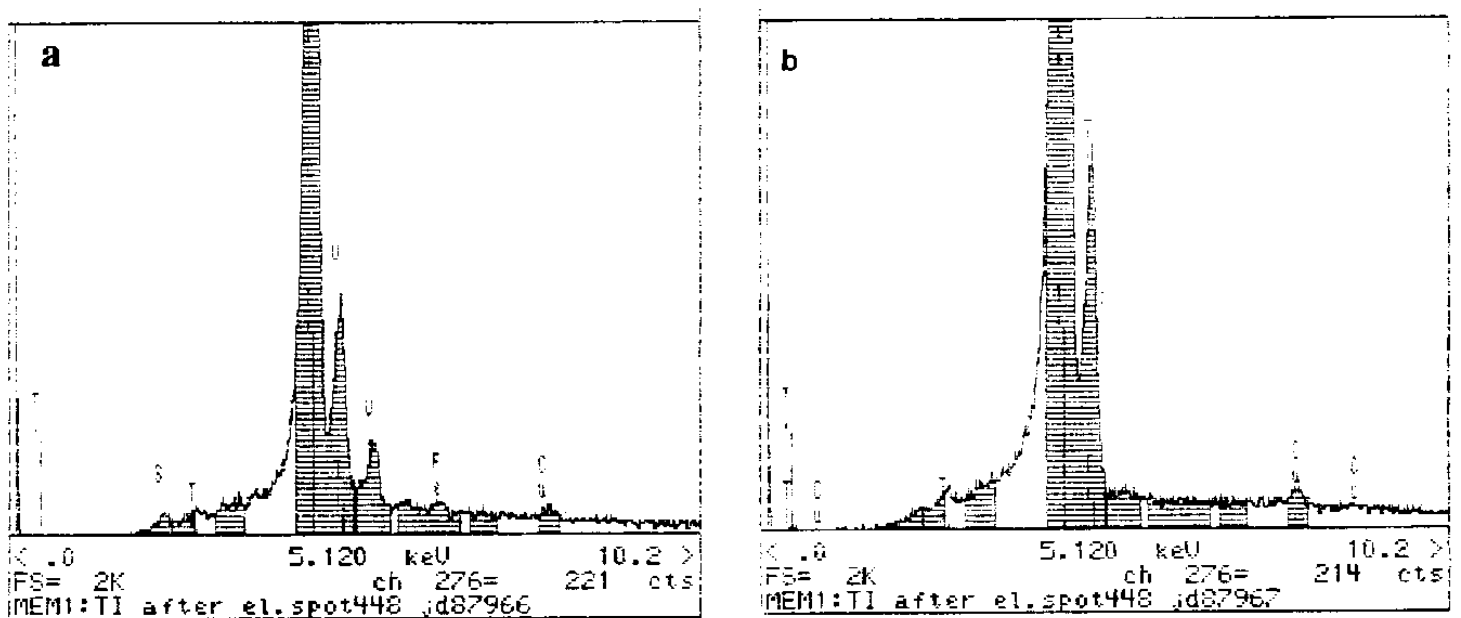


Fig. 8. EDS spectra (a) and (b) from points (a) and (b), respectively, in Fig. 7.