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Research Article

Effect of Recrystallization on Heat Output and Surface Composition of Ti and Pd Cathodes*

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Abstract

The microstructure of Pd and Ti foils was altered by cold rolling followed by heating at temperatures up to ∼700°C. The surface topography and microchemical composition of these foils was studied before and after electrolysis with heavy water electrolyte. Temperature measurements during electrolysis showed that Ti and Pd cathodes which had been heated to ∼700°C gave about 1W excess power relative to a control.
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1. Introduction

It is well known that the microstructure of metals can be altered by deformation which produces point defects (vacancies and interstitials) and line defects (dislocations). Crystal size can vary from single crystals to nanocrystals. The presence of defects and grain boundaries results in slight expansion of the crystal lattice which may enhance diffusion of elements such as hydrogen and deuterium into titanium and palladium, thus increasing the rate and degree of loading. This may increase the excess thermal power produced during electrolysis of heavy water–sulfuric acid electrolyte with Ti or Pd cathodes. The purpose of this research was to determine if heating at elevated temperatures after cold rolling affects the thermal output and surface composition produced during electrolysis with Ti or Pd cathodes.

In a collaborative research effort between scientists at ENEA and SRI International, it has been shown that annealing palladium foil at temperatures between 800 and 1100°C increases the maximum D/Pd loading ratio by reducing the internal stress generated during deuteron sorption by the Pd lattice [1]. Annealing cold rolled metal foils such as Pd and Ti over a Bunsen burner flame should produce a similar reduction in the stress field via recrystallization. The effect of this process on excess enthalpy production, surface morphology, and elemental composition of Pd and Ti cathodes was studied herein.

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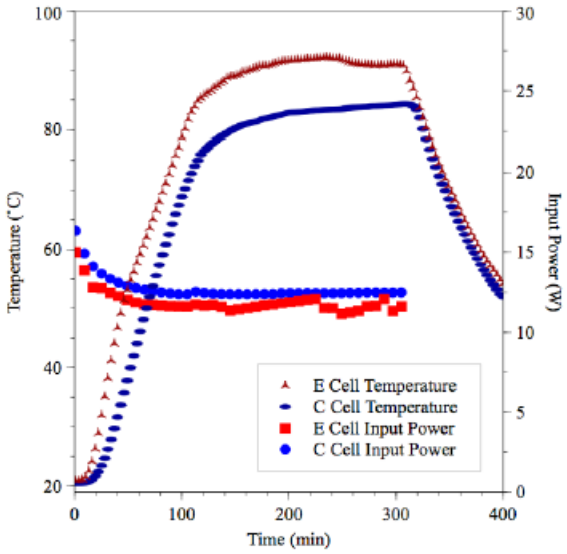

Figure 1. Temperature and input power evolution of an experimental (E) cell containing a thermally treated titanium cathode and a control (C) cell containing a Pt cathode.

2. Experimental

Ti foil (Alfa Aesar stock #43676, 99.99%, metals basis) and Pd foil (Alfa Aesar stock #11514, 99.9%, metals basis) were cold rolled from 0.5 mm thickness to about 0.3 mm thickness. Strips (10×30 mm^2) were # 3 cut from the cold rolled foils to be used as cathodes during electrolysis. The electrolyte consisted of 1.5 M H_2SO_4 (Fisher Scientific, lot #050994) in D_2O (Aldrich stock #14764, 99.8% isotopic).

Two cells were constructed in order to determine if cathodes with recrystallized microstructure are effective in producing excess thermal power. A cell with a cathode made from cold rolled Ti was crimped to a Pt wire (Alpha Aesar stock #10285, 99.95%). A control cell was identical except that its cathode was a Pt foil (Alfa Aesar stock #11509 99.99%). Each cell used a Pt foil anode and the same electrolyte.

Recrystallization was achieved by heating the cold rolled foils for 40 min at an average temperature of $\sim$700°C with a Bunsen burner, after which a recrystallized Ti foil was crimped to the Pt cathode wire. Electrolysis was performed with constant cathode current density of about 0.3 A/cm^2. Cell voltage and temperature were monitored with an automated data acquisition system.

3. Results

The data for the thermocouples which were attached to the outsides of the cells, close to the cathodes, is shown in Fig. 1, along with the power input to each cell. The input power to the control cell (C cell) is slightly higher throughout the experiment than the input power to the experimental cell with the recrystallized Ti cathode (E cell). Even though the E cell received less power, its temperature was higher than that of the C cell throughout the experiment. The peak E Cell temperature was about 92°C, and the peak C cell temperature was about 82°C. These peaks were reached after about 200 min of electrolysis.

The input power fluctuations to the E cell were caused by a loose connection to the cathode wire. Note that there

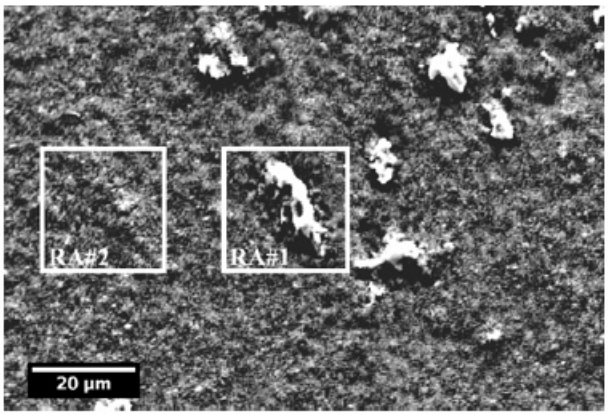

Figure 2. Surface topography of a cold rolled Ti substrate after 40 minutes of heating at 700°C over a Bunsen burner.

is less input power to the E cell than to the C cell throughout the entire run. Even so, the E cell produced about 1W of thermal power more than the C cell.

A second round of electrolysis was conducted using the same electrodes in order to test if the results obtained with this system were repeatable. The recombination catalyst was no longer effective after the first round of electrolysis, so it was replaced in both cells, and additional electrolyte was added to bring the cells to their initial electrolyte levels. The data obtained from this second experiment gave nearly identical results as the first.

A third experiment was conducted using the same electrodes. The recombination catalyst was replaced and the electrolyte was replenished before this run was made. This experiment did not replicate the first two. The maximum temperature was about 100°C for the E cell and 85°C for the C cell. The reason why the third run did not replicate the first two may be because the Ti cathode in the E cell slowly dissolved, thus reducing the surface area. Higher power input was required to maintain the constant current.

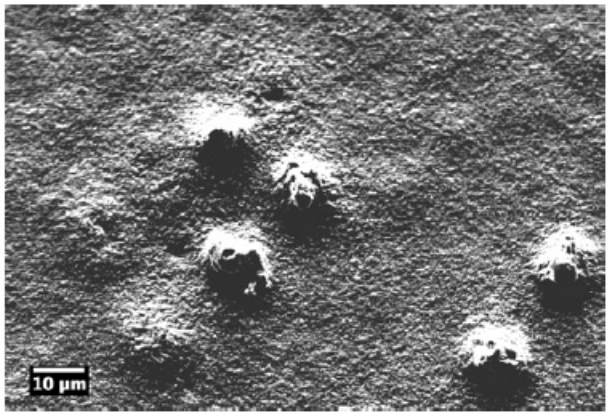

Figure 3. Surface topography of a titanium cathode after cold rolling, heating, and electrolysis in H_2SO_4/D_2O.

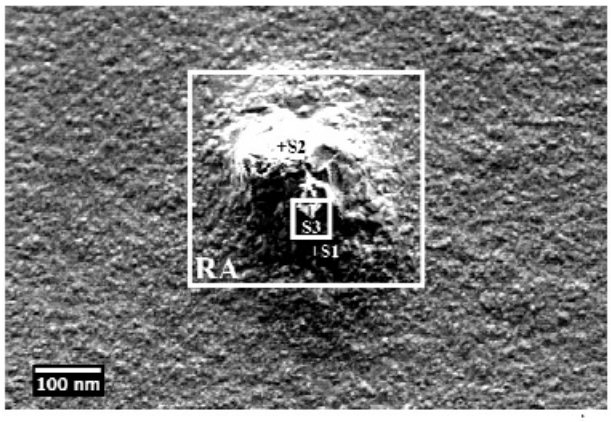

Figure 4. SEM image of a feature commonly found on the surface of a cold-rolled, heated titanium cathode following electrolysis in acidified heavy water.

The result was higher E cell temperature, which vaporized about 30 ml of the electrolyte. This loss made it impossible to calculate excess power accurately.

4. SEM and EDS Characterization

Using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS), we studied the surface topography and microcomposition of the thermally treated cathodes both before and after electrolysis. Figure 2 shows the typical surface topography of a titanium cathode after heating but before electrolysis.

EDS data was collected from the reduced areas outlined in Fig. 2. The EDS scan obtained from the center of the image (RA#1) contains about 2 at.% Fe, along with O, C, and Ti, whereas the reduced area to the left (RA#2) contains only O, C, and Ti (Table 1).

Figure 3 shows the surface topography of a Ti cathode that had undergone cold-rolling, followed by 40 min of heating at $\sim$700^{o}C, and electrolysis. There are three similar pits (*black*) about 50 μm diameter, with white rims which protrude above the surface. The surface eruptions have similar size and shape.

EDS spectra were taken from an eruption on a Ti cathode after cold rolling, heating, and electrolysis (Fig. 4). Spectra were obtained from the whole area, the reduced area (RA), the black spot S1, the white spot S2, and the triangular area in the small square near the center labeled S3 (Table 2). The detected elements consisted mainly of C, O, and Ti. Anomalous V was found in four of the five spectra at the 0.1 at.% level. Anomalous V, Cr, Fe, and Ni were found in the triangular particle within the small square near the center of the figure. Fe was at the 0.3 at.% level, and the other elements were at the 0.1 at.% level.

Table 1. Atomic composition of RA#1 and RA#2 in Fig. 2

Element	Atomic (%) composition reduced area #1	Atomic (%) composition reduced area #2
C	11.79	16.73
O	77.79	72.05
Ti	8.54	11.22
Fe	1.88	0

We performed similar experiments using Pd foils instead of Ti and obtained similar results. At steady state, the temperature of the cell with a heated Pd cathode was about 7°C higher than that of the control. With the same input power, this means that the heated Pd cathode was producing about 1 W more power than the control.

The topography of a Pd cathode after heating but before electrolysis is shown in Fig. 5a. It appears that surface melting has occurred, leaving a network of pores. Since the melting point of Pd is 1549°C and the Bunsen burner flame does not reach such temperatures, we speculate that a diffusion based process is responsible for the formation of the porous microstructure in Pd, namely spinodal decomposition [2, 3].

It is apparent that the heating of Pd over a Bunsen burner flame produces a high surface area, porous topography. More over, this morphology is stable since it has clearly maintained its structure even after 22.5 h of electrolysis at a current density of 340 mA/cm^2 (Fig. 5b). The white dots on the palladium surface seen in Fig. 5b are electroplated platinum deposits, which come from the dissolution of the anode.

Figure 6 shows another example of porous surface microstructure on a Pd cathode which had been heated in a Bunsen burner flame, then electrolyzed for 14.5 h. The pores seem to be concentrated in strands which meander over the surface. The square area in the center of the micrograph is shown enlarged in Fig. 6b, which has features suggesting

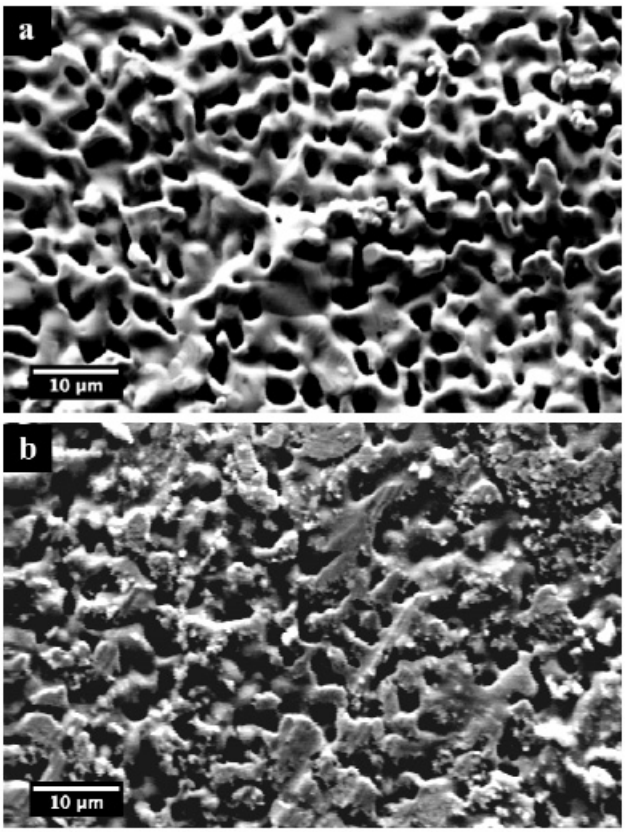

Figure 5. Surface topography of a Pd cathode after heating for 40 min under a Bunsen burner flame (a) before and (b) after electrolysis in H_2SO_4/D_2O.

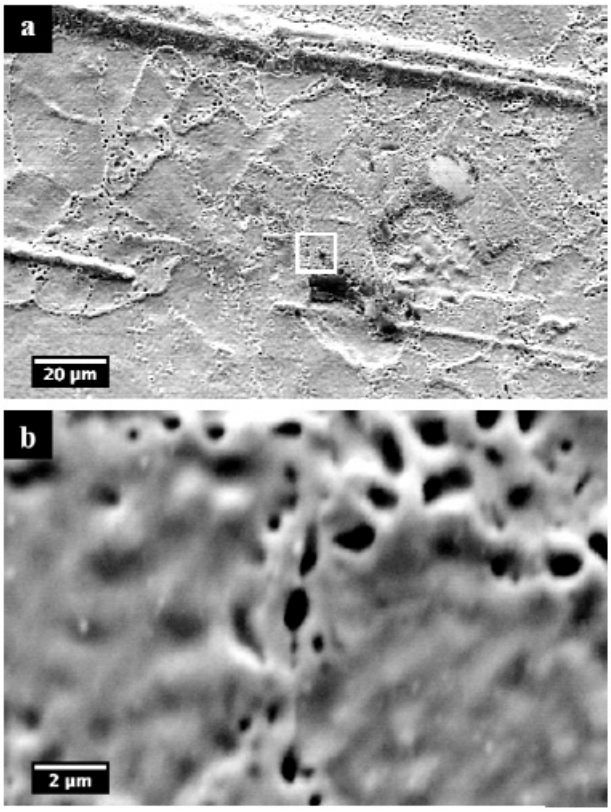

Figure 6. (a) Low magnification and (b) high magnification SEM image of a heated Pd sample following electrolysis in H_2SO_4/D_2O.

surface melting.

Figure 7 shows another view of a porous Pd cathode after electrolysis. Two of the pores were analyzed with the results given in Tables 3 and 4. Both contain significant amounts of Ag, which is consistent with our previous results [4].

Table 2. Atomic composition of the labeled regions in Fig. 4

Element	Atomic (%) composition reduced area	Atomic (%) composition black S1	Atomic (%) composition white S2	Atomic (%) composition whole area	Atomic (%) composition white triangle S3
C	26.71	43.78	35.72	22.25	41.21
O	64.60	52.93	59.55	68.92	52.60
S	0	0	0	0	0.04
Ti	8.69	3.23	4.67	8.73	5.60
V	0	0.06	0.07	0.11	0.08
Cr	0	0	0	0	0.10
Fe	0	0	0	0	0.33
Ni	0	0	0	0	0.04

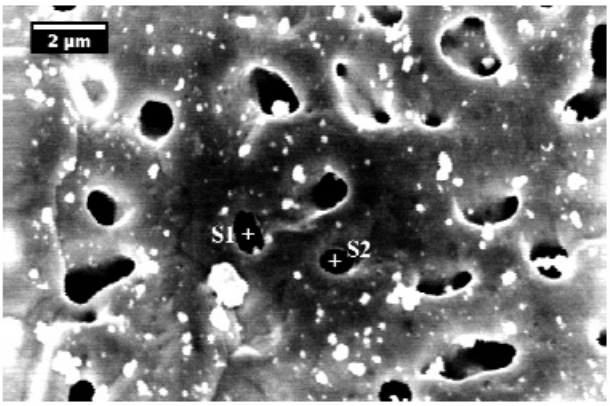

Figure 7. SEM image of a cold-rolled, heated Pd substrate following electrolysis in H_2SO_4/D_2O.

Table 3. Atomic composition of pore S1 in Fig. 7

Element	Weight %	Standard deviation	Atomic %
C	5.12	0.42	33.67
Al	0.7	0.16	2.03
Pd	70.76	1.52	52.51
Ag	7.04	1.68	5.15
Pt	16.39	0.79	6.63

As a final example, Fig. 8 shows the locations on the surface of a thermally treated, electrolyzed Pd cathode from which EDS spectra were obtained.

Quantitative results suggest that three of the five regions contain significant quantities of silver, with the highest concentrations located within pores (Table 5). Anomalous Ag is found in the black and gray features, but not in the

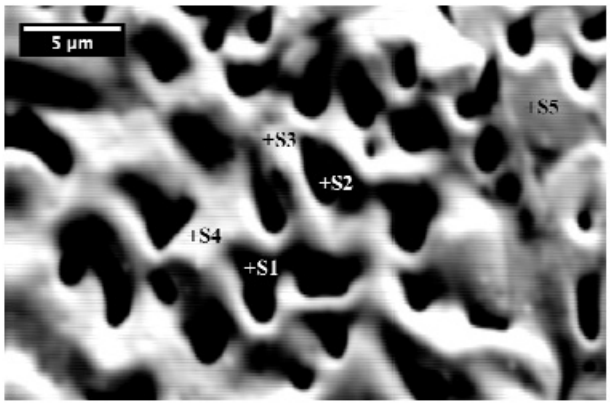

Figure 8. SEM image of the concave side of a heated palladium cathode after 14.5 h of electrolysis.

Table 4. Atomic composition of pore S2 in Fig. 7

Element	Weight %	Standard deviation	Atomic %
C	0.82	0.26	7.18
Pd	80.49	1.84	79.12
Ag	8.49	1.92	8.23
Pt	10.20	0.74	5.47

white features.

A primary objective of this research was to determine if there is an optimum time of heating at 700°C that produces a microstructure which maximizes excess heat during electrolysis. The results obtained for Pd cathodes are given in Table 6. Heating Pd for 40 min at 700°C gave 7°C higher steady-state temperature than no heating.

5. Discussion

The microstructure of the cathode in low energy nuclear reaction (LENR) studies is an important factor in loading hydrogen isotopes into the host lattice. In the case of nanocrystals, the goal is to prevent sintering of the microscopic particles so that a large surface area to volume ratio is maintained.

Cold rolled Ti foils, melting point 1668°C, and cold rolled Pd foils, melting point 1549°C, were used in this research. The goal of heating was to recrystallize the foils to form a new set of microscopic crystals with a large surface area to volume ratio.

Although the data are few, it seems that heating the foils for 40 min at 700°C produces microcrystals and unexpected microporosity which serve to increase excess heat and reproducibility for both Ti and Pd. In addition we continue to observe anomalous Ag in our EDS spectra, such as we reported previously [4].

It was suggested that the observed surface morphology is due to a compound of Pd, O, and C which has a low melting point [5]. Such a compound could form at elevated temperature if the free energy change is favorable. Rapid cooling to ambient would preserve the surface morphology in the form which was produced at elevated temperature.

6. Conclusion

This study shows that it is possible to enhance excess heat from metals such as Ti and Pd by thermal treatment to produce microstructure such as porosity which is favorable to diffusion of gases into the metals. Reproducibility of results may also be increased.

Acknowledgment

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Table 5. Atomic composition of various spots on the sample shown in Fig. 8

Element	Atomic (%) composition black S1	Atomic (%) composition black S2	Atomic (%) composition white S3	Atomic (%) composition white S4	Atomic (%) composition gray S5
C	19.42	23.80	36.82	42.11	26.34
O	36.05	23.34	24.55	24.04	30.37
Pd	37.55	45.18	31.49	28.36	35.55
Ag	1.49	3.78	0	0	0.59
Pt	5.49	3.90	7.14	5.49	7.14

Table 6. Effect of recrystallization heat treatment of palladium cathodes on cell temperature during electrolysis

Duration of thermal treatment (minutes at ∼700°C)	Steady-state temperature during electrolysis (°C)
0	64
20	65
40	71
60	68

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