Metallurgical Characterization of Pd Electrodes Employed in Calorimetric Experiments Under Electrochemical Deuterium Loading

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Abstract

A systematic approach has been followed in the production and characterization of Pd foils to be used in excess heat production experiments [1][2][3]. Starting with a metal foil as supplied, palladium samples have been fabricated and characterized in a step by step process, and then subjected to electrolysis deuterium loading. The characterized metallurgical properties include the main grain size, the grain boundary, the material Vickers hardness, and the crystal grain orientation. Electrochemical properties that are recorded include the D/Pd loading ratio and the D/Pd low current loading ratio. A suitable correlation parameter has been defined and correlations have been found between excess heat production and individual properties; i.e. the mean grain size, grain boundary, material hardness, crystal grain orientation, deuterium loading and low-current deuterium loading level.

Introduction

A great deal of experimental evidence indicates that the reproducibility of excess heat production is strongly controlled by the cathode's material properties. To achieve deeper understanding of the phenomenon, a systematic characterization of the metallurgical properties and loading behaviour of Pd cathodes used in excess heat experiments at different laboratories (ENEA, SRI, Energetics Technology), has been performed. A central role in the improvement of the study is the development of a tool for experimental data organization and storage; i.e. a database including all the information collected for each sample. The data is rigorously organized and easily retrieved and compared.

Data analysis aimed to look for correlations with excess heat production. A statistical approach has been followed, as the role played by each material-related issue is not known yet, and an exhaustive theoretical explanation has not been devised.

Experimental

Starting with the metal foil from the supplier, palladium samples have been produced and characterized in a step by step process before being subjected to an electrolysis deuterium loading experiment.

Cathode Manufacturing

Cold rolling and annealing create an optimized metallurgical structure of the material, which increases deuterium loading. The raw starting material was palladium foil 1 mm thick able to reach a loading ratio of about 0.75 - 0.8 hydrogen/palladium atomic ratio.

The initial treatment was done in two steps:

(1) Cold rolling of the raw material produces Pd foils 50 microm thick.
(2) Annealing at temperatures ranging from 800 to 900°C for about 1 hr.

The resulting foils are rectangular, about 20 mm long and 10 mm wide, with a thickness of about 50 μm. These strips are cut into 40 mm long pieces, to make cathodes with appropriate dimensions. Then the samples are chemically etched using nitric acid and aqua regia. This is done to clean impurities from the surface which can contaminate it during the cold rolling and annealing, and also to activate the surface, making it easier for hydrogen to diffuse into the metal lattice. From a metallurgical point of view such treatment reveals material surface morphology, allowing the SEM observation of the grain dimension distribution in the sample. Surface chemical etching is also one of the suitable methods to obtain the required surface roughness.

Cathode Characterization

Because the origin and preparation of the cathode is crucial to the outcome of the experiment, each step in the process should be recorded for each sample. We do this with a protocol for the sample designation. For example, the cathode designated *L54(189-227)RAEF* indicates the following: *L54* is the rolling run; *(189-227)* indicates the sample position inside the original rolled stripe; *R* stands for “rolling performed”; *A* for “annealing performed”; *E* for “etching performed”; and *F* is the deuterium loading specification (i.e. in which electrochemical cell the sample was placed).

Metallurgical properties that have been characterized include the most common grain size found in the sample, the grain boundary, Vickers hardness, and the crystal grain orientation. Because the samples in this study are polycrystalline, the chemical behaviour of the surface is not homogeneous, and strictly dependent on the grain crystallographic orientation.

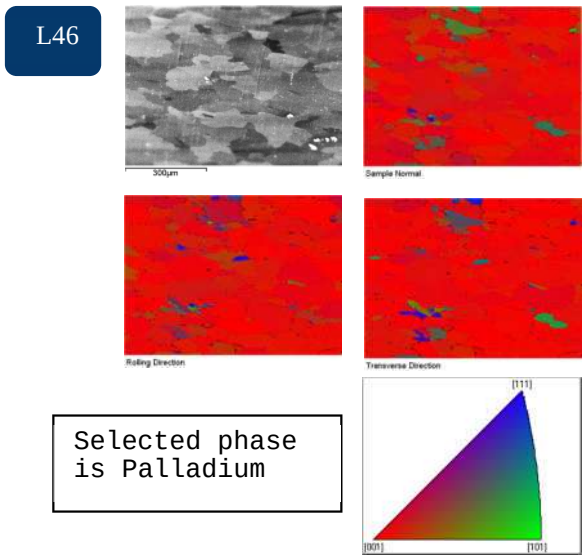

Figure 2.1. Grain orientation distribution as revealed by EBDS on L46 Pd sample

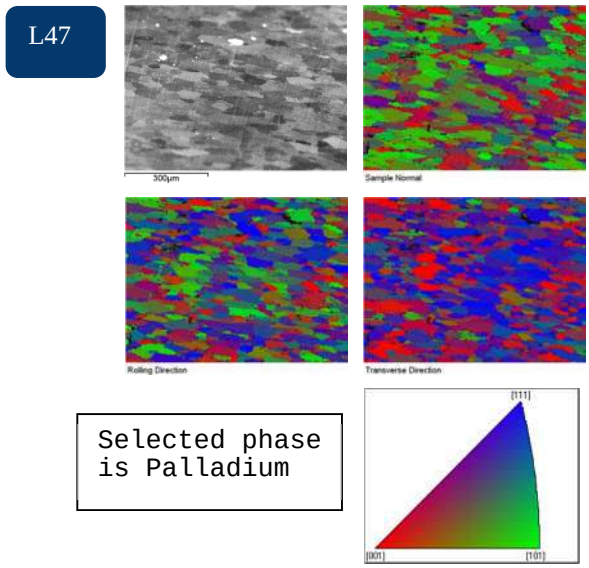

Figure 2.2. Grain orientation distribution as revealed by EBDS on L47 Pd sample

Excess heat experiments

After the Pd samples are fabricated and characterized from a metallurgical point of view, they are used as cathodes in electrochemical cells, which are placed inside a calorimeter. The metal lattice is loaded with deuterium to see if excess heat production occurs.

All the samples used in this study gave a D/Pd loading ratio with values ranging from 0.9 up to about 1.

The calorimetric study allowed us to understand that not only loading but also intrinsic properties of the material controlled the reproducibility of excess power. This evidence prompted us to establish a database of material properties.

Database

The custom- developed database includes all relevant characterization parameters. A typical record is shown in Fig. 3.1. It includes the sample name and its manufacturing specifications, and also the results of materials measurements, together with SEM and AFM images.

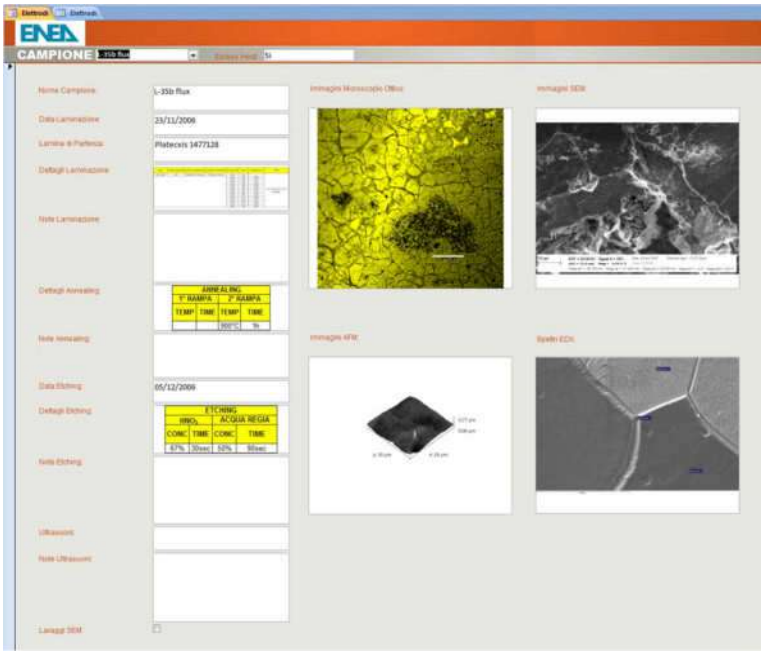

Figure 3.1. A typical database record

Analysis

After systematically characterizing the cathodes, and collecting and organizing the data, a statistical analysis was performed to look for correlations with excess heat. To quantify the correlation a *"degree of correlation" (g)* between a selected property (*f)* and the excess heat occurrence (*h)* has been defined as:

$$g = \frac{\langle f \times h \rangle}{\sqrt{\langle f \rangle^2 \langle h \rangle^2}}$$

Where g=1 then there is full correlation between the selected property and the excess heat production; where g=0 there is no correlation.

Results and Discussion

Figures 4.1 through 4.6 show the histograms of each of the material properties investigated in this work, together with the indication of excess heat production (shown in the graphs with the thinner bars).

It can be seen from these figures that some properties are well correlated with the excess heat production. This is particularly evident in Fig. 4.2, showing that most of the samples giving excess heat have well defined grain boundaries, while samples in which grain boundaries are not clearly identifiable by microscope inspection, in most cases did not produce excess heat.

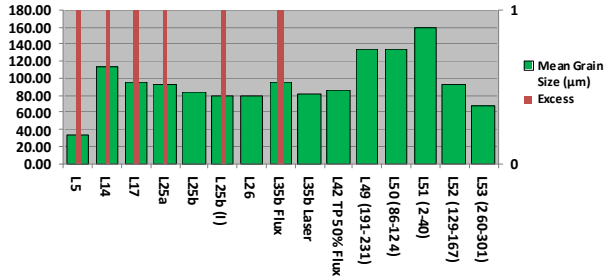

Figure 4.1. Mean grain size correlation with excess heat occurrence

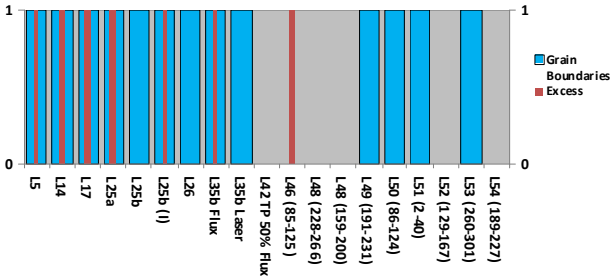

Figure 4.2. Grain boundary correlation with excess heat (1=correlation evident, 0=not evident)

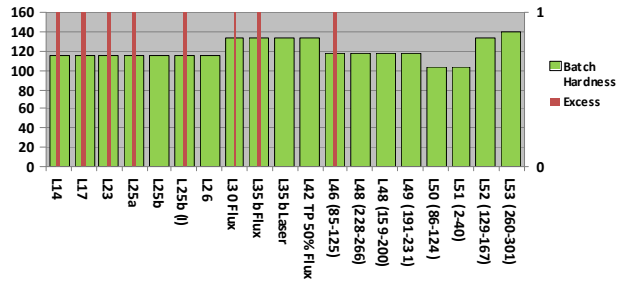

Figure 4.3. Vickers hardness (units areMPa) of batch correlation with excess heat

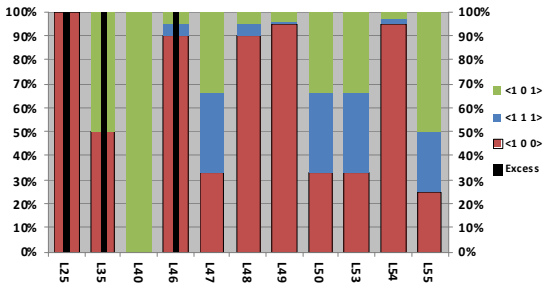

Figure 4.4. Grain crystal orientation correlation with excess heat

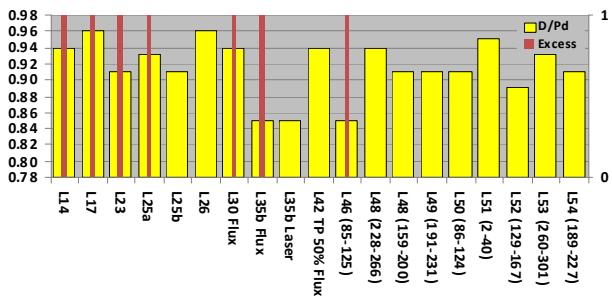

Figure 4.5. D/Pd loading ratio correlation with excess heat

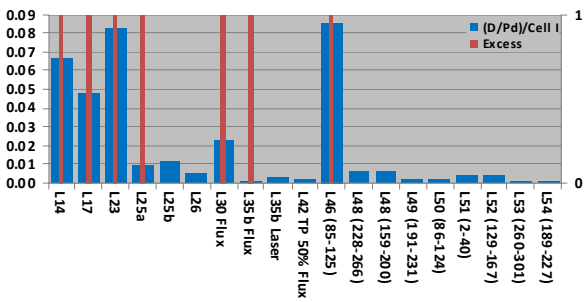

Figure 4.6. Low current D/Pd loading correlation with excess heat (units are mA^{-1})

Figure 4.1 shows the mean grain equivalent radius (units are microns), as it has been measured from the SEM images, by counting the number of grains present in a fixed area.

Figure 4.3 shows that excess heat occurred with more statistical probability with samples which have a Vickers hardness of 120 MPa. The Vickers hardness is measured on the

palladium lot as received. Different hardness values indicate different elastic properties and different impurity content in the original material.

In Fig.4.4 the results of crystal grain orientation are reported. The ordinate axis indicates the percentage of the sample volume which is oriented along a particular crystallographic direction. Three sets of data have been reported, one for each of the main lattice planes: <100>, <101>, <111>. Although the results are not statistically significant because the ensemble of samples on which crystallographic data have been available is limited, the graph shows that only samples having more than 50% <100> orientation gave excess heat, suggesting that <100> orientation is a necessary condition for excess heat to occur.

The last two figures (Fig. 4.5 and 4.6) show data on deuterium loading. In Fig. 4.5 the ordinate axis indicates the values of the D/Pd atomic ratio determined with four point probe resistivity measurements and the Baranowskii – McKubre curve. This is measured during electrolysis. The results confirms what has already been described in literature, that a D/Pd ratio higher than 0.85 is a necessary condition to obtain excess heat. It should be noted, however, that all the samples considered have a D/Pd ratio higher than 0.85; the correlation parameter *g* value would be much higher if samples below the loading threshold had been considered.

Fig. 4.6 gives insight into a more unexplored result. The histogram shows the ratio between D/Pd atomic ratio (also referred as the “maximum loading”) and the electric current that was flowing through the cell when that loading was obtained. McKubre identified two types of excess power production: Type A, excess begins after several days of electrolysis and depends on the current density; and Type B, excess begins soon and does not always depend the current density. [4] The figure shows that when excess heat is produced, a high level of deuterium loading was generally obtained at low electric current (see samples L14, L17, L23, L46); exceptions are samples L25a and L30Flux, which both gave excess heat of type B, while all other samples gave excess heat of type A.

Table 4.1. Correlation factor g value for measured properties of the Pd samples

	Hardness	Mean Grain size	Grain boundary	Grain Crystal Orientation			D_2 Loading	Low Current D_2 Loading
				<100>	<101>	<111>		
Correlation Factor (*g*)	***0.65***	***0.64***	***0.63***	***0.62***	***0.23***	***0.46***	***0.60***	***0.81***

Conclusions

Starting with metal from commercial suppliers, Pd cathodes have been produced and characterized systematically, by performing measures on their metallurgical and electrochemical properties.

The experimental data have been filed and stored in a database.

Suitable correlation parameters have been defined and correlations have been found between heat excess production and individual properties; i.e. the mean grain size, grain boundary, material hardness, crystal grain orientation, deuterium loading and low current deuterium loading level.

Multiple-regression data analysis could also be advantageously applied to our data, because the number of samples in the database is increasing.

References

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4. V. Violante, F. Sarto, E. Castagna, M. Sansovini, S. Lecci, D.L. Knies, K.S. Grabowski, G.K. Hubler, *"Material Science on Pd-D System to Study the Occurrence of Excess of Power*", in these proceedings