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Development of Poison Resistant Palladium Alloys for Hydrogen Processing

K. L. Shanahan

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Development of Poison Resistant Palladium Alloys for Hydrogen Processing

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EXECUTIVE SUMMARY

Synthetic capability to make Pd alloys at SRNL has been established by the synthesis of three test foils of nominal chemical formula $\text{Pd}_{0.9}\text{Rh}_{0.1}$, $\text{Pd}_{0.86}\text{Rh}_{0.1}\text{Y}_{0.04}$, and $\text{Pd}_{0.84}\text{Au}_{0.15}\text{Y}_{0.01}$. These alloy foils were produced by melting appropriate amount of the pure elements in a tube furnace under argon, followed by rolling the resultant buttons to 150-200 micron thicknesses. Alloy quality was assessed by measuring the degree of crystallinity and contaminant content by X-ray diffraction (XRD) and the level of chemical homogeneity by Energy Dispersive X-ray (EDX) analysis spectra and elemental maps coupled with Scanning Electron Microscopy (SEM). Hydrogen isotope absorption/desorption behaviors were also characterized by obtaining hydrogen and deuterium isotherms.

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LIST OF ABBREVIATIONS

| | |
|------|------------------------------------|
| SRNL | Savannah River National Laboratory |
| SEM | Scanning Electron Microscopy |
| EDX | Energy Dispersive X-ray (Analysis) |
| XRD | X-Ray Diffraction |

1.0 Introduction

Palladium (Pd) alloys are formed by adding a wide variety of alloying elements to Pd. Alloys typically show altered hydrogen absorption/desorption characteristics that can have benefits to hydrogen isotope processes. One aspect of this is poison resistance. Several gases or contaminants in gases can absorb on Pd-alloy materials and severely inhibit hydrogen absorption or desorption properties. Two of particular interest are carbon monoxide (CO) and sulfur (S). Sulfur can be found in many gaseous compounds, but perhaps the most recognized is hydrogen sulfide (H₂S) or rotten-egg gas. Exposing Pd alloys to either of these two compounds results in an almost complete inhibition of hydrogen absorption capability. CO can normally be removed by elevating the alloy's temperature to over 300 °C, but removal of surface S (formed by decomposition of H₂S) is difficult to achieve. Typically, in surface science studies the S is sputtered away with an argon ion gun or dissolved into the bulk by heating. The latter approach however, will alter the alloy characteristics in the same fashion as any other added alloying element.

Two uses of Pd at SRS include Pd supported on kieselguhr, used for separation of hydrogen isotopes, and as a Pd alloy in diffuser membranes to extract H isotopes from various gas streams. It would be advantageous to have alloys that resist poisoning, as this allows for longer process lifetimes and the possibility of lower temperature operation.

A SRNL project was initiated to establish small quantity Pd alloy synthesis capabilities at SRNL. That goal has been achieved at this point in time. Three Pd alloys have been prepared to date, with their initial characterization being completed. This report will describe the results.

2.0 Experimental Procedure

There are several methods available to the synthetic alloy chemist for preparing new metal alloys. Generically some can be listed as: melting (arc or furnace), ball milling, salt reduction, co-deposition, and others. The key was to decide which would present a user-friendly method for multiple alloy preparations in rapid sequence. After some consideration, it was determined that a tube furnace presented the best route to alloy synthesis via high-temperature melting. Accordingly, some test runs were initiated.

The first run was a simple 10% mix of Rh in Pd (nominal chemical formula Pd_{0.9}Rh_{0.1}). This would produce material with which some prior experience existed and thus could serve as an initial test case of the melting procedure's applicability. The initial run was quite successful, producing a homogeneous alloy with characteristics that nearly matched similar materials prepared in the prior research¹⁻⁵ by a Univ. of Vermont chemistry professor, Prof. Ted Flanagan, a world expert in Pd-H and Pd alloy-H chemistry. The second alloy prepared was to be a Pd-Rh-Y alloy. The Y was added because the prior research showed it gave resistance to CO poisoning and had a high H solubility, which leads to good membrane permeability. But the alloy turned out to have significant O content (as Y₂O₃), most likely because of poor experimental protocol, and did not appear to form a homogeneous alloy. An attempt was made to re-melt this alloy to improve the homogeneity, but the resulting melt did not appear to have fully melted. However, it should be noted that (a) the prior work for SRNL by Prof. Flanagan involved oxidizing the alloying elements to certain extents to develop poison resistance, and (b) Y alloys are often disordered and thus may appear to be poorly alloyed, so the Pd-Rh-Y alloy may actually have useful properties when exposed to poisons. The third alloy prepared was a Pd-Au-Y alloy. Pd-Au alloys have been shown in the literature^{6,7} to have resistance to S poisoning, although the Au content needs to be at or above 15 at%. It was hoped that combining the Y and Au might offer both S and CO resistance and good permeability at the same time. Initial characterization results are presented below.

Samples were prepared by placing pure elements together in a MgO crucible, typically ~5 g. total weight, which then was wrapped in Ta foil and placed in a 1700 °C tube furnace. The furnace tube was constructed out of alumina, which required that some positive pressure was maintained at the higher melt temperatures to prevent sagging. Therefore, after placing the crucible inside the alumina tube, the tube was capped, evacuated and purged three times with house Ar. After the final purge, the Ar was refilled and a low flow through the tube established, whereupon the heating ramp was initiated. Controlled heating is also required

to minimize thermal stresses during the severe temperature change from room temperature up to ~1600-1700 °C and back. Once the samples had been melted, they were held at that temperature for roughly 60 minutes to allow for optimal alloying to occur. Once the sample had cooled back to room temperature, it was removed from the furnace and the crucible. With the Pd—10%Rh alloy, the alloy wetted the crucible and the crucible had to be destroyed to extract the sample. That process left small MgO particulates attached to the Pd—Rh alloy. The Pd-Rh-Y alloy did not wet the crucible, instead forming a marble that easily fell out of the crucible. The Pd-Au-Y alloy likewise did not wet the crucible and was treated similarly to the Pd-Rh-Y alloy.

Once the samples were removed from the crucible they were initially flattened with a hammer to a thickness where they could then be rolled thinner. The rolling process was accomplished on a roller with the sample protected from the rolls by thin stainless-steel foils. Once the material had been thinned down a few times, it had expanded geometrically to the point where a smaller piece of it was separated from the bulk and thinned to final thickness. Thickness was measured at several spots on the resulting foil with calipers and averaged 150-200 microns.

Samples were characterized by SEM/EDX analysis, with elemental mapping, XRD, and by determining hydrogen isotope isotherms at various temperatures. Approximately 1-2 grams of the foil was cut up into small squares capable of fitting through the ¼" Cajon™ 4-VCR fittings used on isotherm sample cells. Other pieces of the foils were submitted for XRD analysis and for SEM/EDX analysis to measure the degree of alloy homogeneity. The Pd-Rh and Pd-Au-Y alloys were found to be homogeneous with sharp peaks in the XRD spectrum, although the Pd-Au-Y sample did show traces of Y₂O₃ in the XRD and possible segregation in the EDX elemental maps (see below). The Pd-Rh-Y sample was very inhomogeneous, particularly with respect to Y and O distributions (see below). Homogeneous hydride materials tend to produce well-defined hydrogen isotherms showing a clear flat plateau region, which marks the transition region between the alpha and beta hydride phases, and this was observed with the Pd-Rh alloy. The Pd-Rh-Y alloy however gave very poorly defined isotherms indicating the sample inhomogeneity. The Pd-Au-Y alloy's isotherms had slightly sloped plateaux but were comparable to literature results on Pd-Au alloys.

3.0 Results and Discussion

XRD Spectra

These Pd alloys are substitutional alloys, which means that the alloying element replaces a Pd atom in the crystal lattice. Thus, with the exception of minor lattice size changes, the crystal structure does not change much and resulting XRD spectra will be very similar.

Figure 1 shows the XRD spectrum of the SRNL synthesized Pd-10%Rh alloy foil. A Pd-Rh foil produced by Prof. T. Flanagan in the prior research project was not available, but a Pd-Rh-V foil was found and submitted for XRD analysis to compare the quality of that spectrum to SRNL synthesized alloys. Superimposed on the SRNL Pd-10%Rh (black) spectrum in Figure 1 is the spectrum of the Pd-Rh-V (green) foil. The two alloys show highly similar spectra with baseline flatness and peak sharpness being quite comparable, indicating that the SRNL preparation technique was producing competitive quality alloys.

Figures 2 and 3 show the XRD spectra for the Pd-Rh-Y and Pd-Au-Y alloys respectively. The nominal composition of the foils are Pd_{0.86}Rh_{0.1}Y_{0.04} and Pd_{0.84}Au_{0.15}Y_{0.01}. Of note are the sharp peaks and flat background of the Pd-Au-Y alloy as contrasted with the very diffuse signals found in the Pd-Rh-Y spectrum. In that spectrum, peaks for Pd (or Pd-Rh alloy) and yttriaite (Y₂O₃) are identifiable, and the 'Pd' peaks fall at the same place as those in Figure 1, likely indicating that a Pd-Rh alloy with trace Y plus Y₂O₃ embedded in it was formed. There appears to be a trace amount of Y₂O₃ in the Pd-Au-Y alloy based on the small XRD peak found.

Pd-Rh Alloy SEM/EDX Analysis

Three regions of the Pd-10% Rh foil were examined by EDX mapping and results are shown below in Figures 4, 5, and 6. In the first (Figure 4) maps for Pd and Rh, the primary alloy elements and Mg and O are shown. The Mg and O likely come from small pieces of the MgO melting crucible, as the Pd-Rh alloy wetted the crucible and had to be forcibly removed from it. The original button was thinned initially by placing between stainless steel (SS) sheets and hammering out. Subsequently, additional thinning was accomplished by passing the SS sheet – Pd-Rh alloy foil several more times through a roller. The process potentially can transfer some SS into the sample. The primary constituents of SS are Fe, Cr, and Ni (not mapped). Si is also a common contaminant, however the map in Figure 6 may be background noise. Fe and Cr however show small concentrations in Figures 5 and 6 indicative of contaminant spots such as would arise from a small piece of SS. Likewise, the Mg and O spots are correlated and likely arise from residual pieces of the crucible. The lines/streaks shown in the SEM photos are likely caused by the rolling process. The sample was not annealed; thus evidence of the cold working remains. Of note is the fact that the Pd and Rh maps show no evidence of irregular distribution, indicating a homogeneous alloy was formed. Figure 7 shows the EDX spectrum obtained from one region of the foil. It indicates that the Pd:Rh ratio is roughly 9:1 as expected (EDX is considered a semi-quantitative analytical technique).

Figure 1. XRD Spectra from SRNL 10%Rh-Pd foil and Flanagan Pd-Rh-V foil

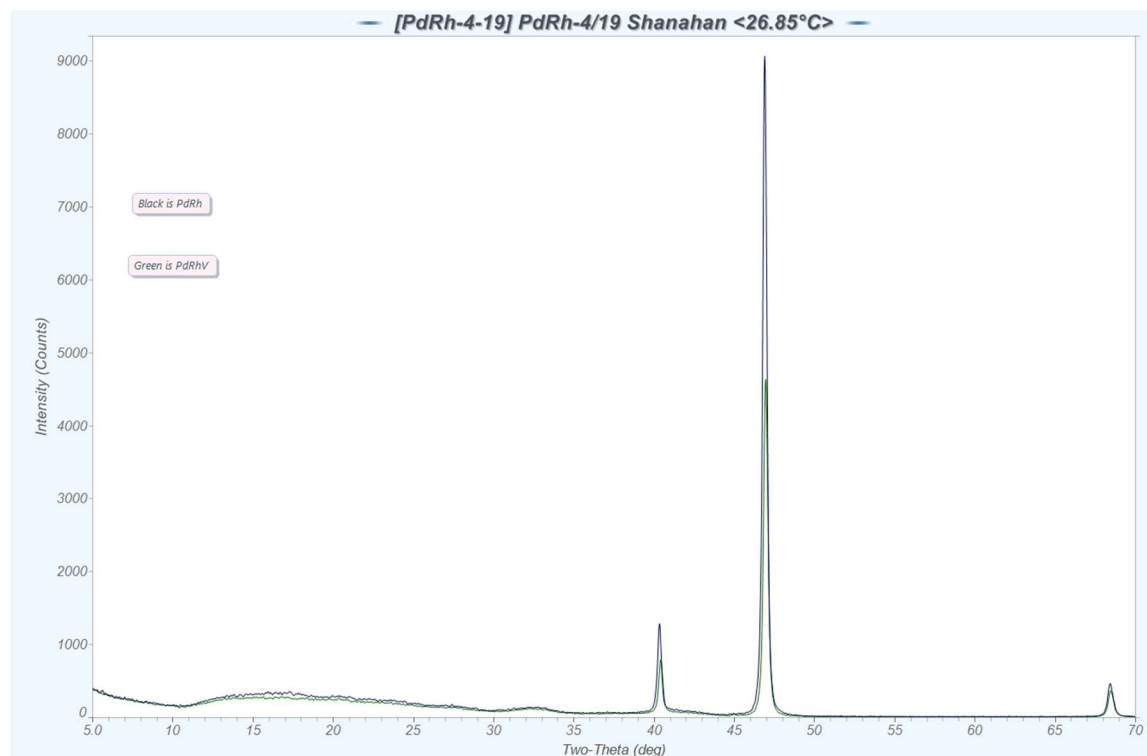


Figure 2. XRD Spectrum from SRNL Pd-Rh-Y foil

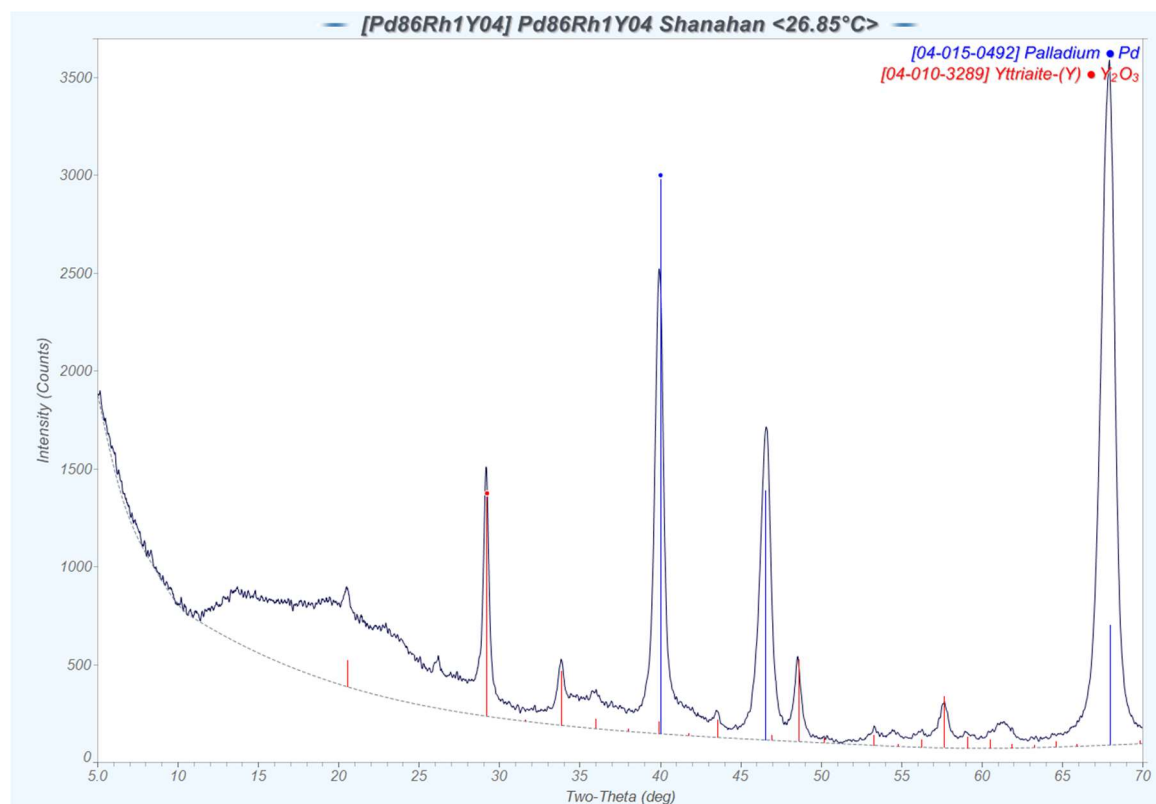


Figure 3. XRD Spectrum from SRNL Pd-Au-Y foil

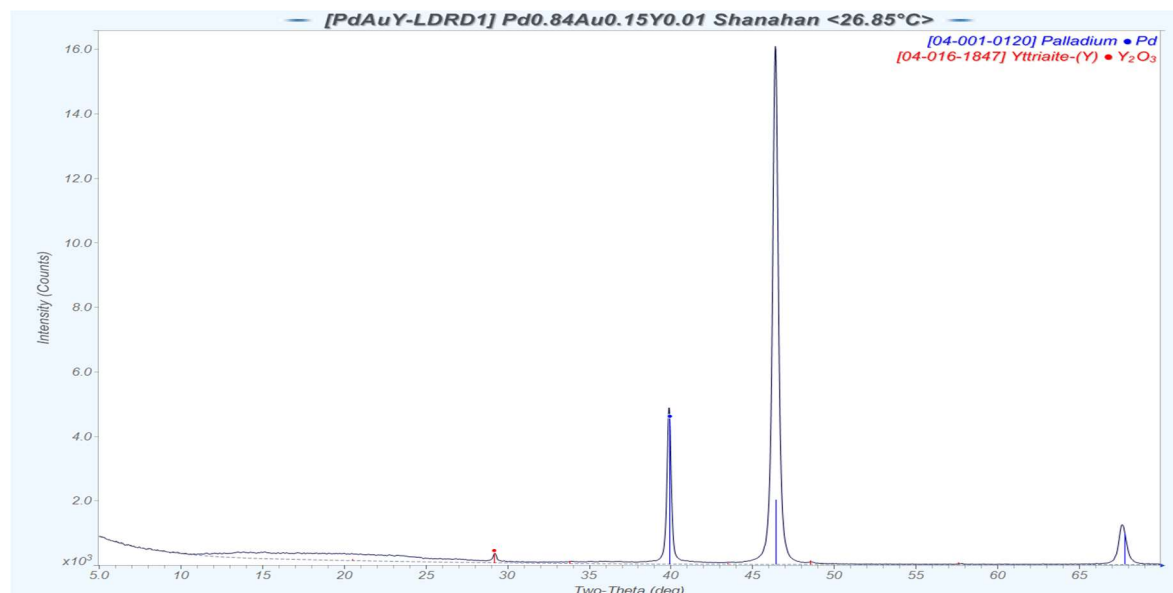


Figure 4. SEM/EDX analysis of indicated region of Pd—10%Rh foil (circled on low magnification SEM photograph of the whole foil piece, lower left). Elemental maps of Pd, Rh, Mg, and O shown.

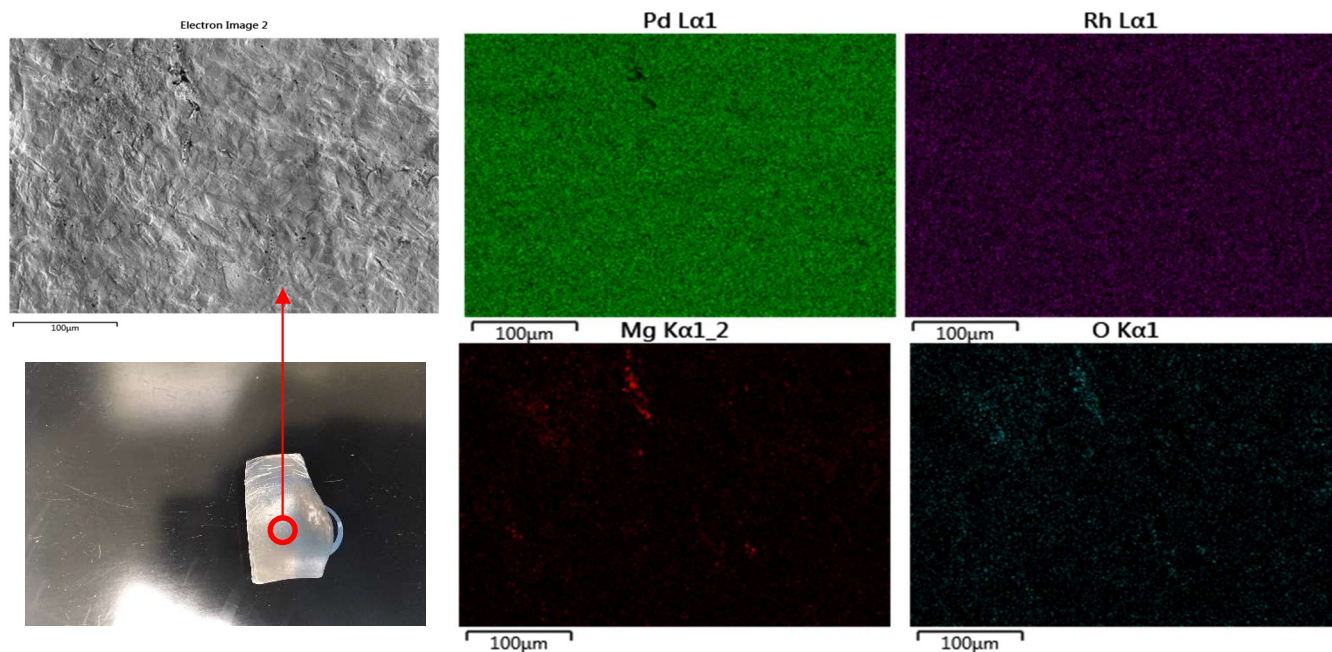


Figure 5. SEM/EDX analysis of second region of Pd—10%Rh foil. Elemental maps of Pd, Rh, Mg, Fe, and O shown.

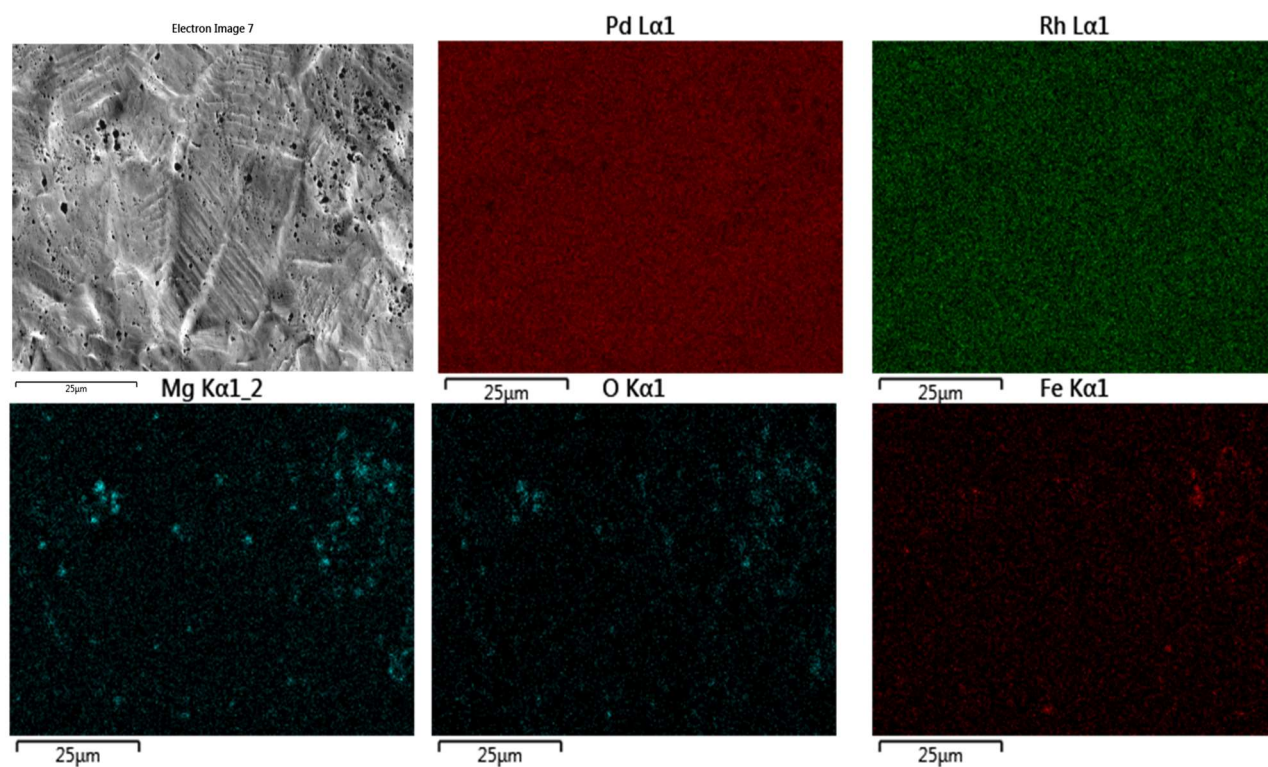


Figure 6. SEM/EDX analysis of third region of Pd—10%Rh foil. Pd, Rh, Mg, Fe, Cr, Si, and O elemental maps are shown.

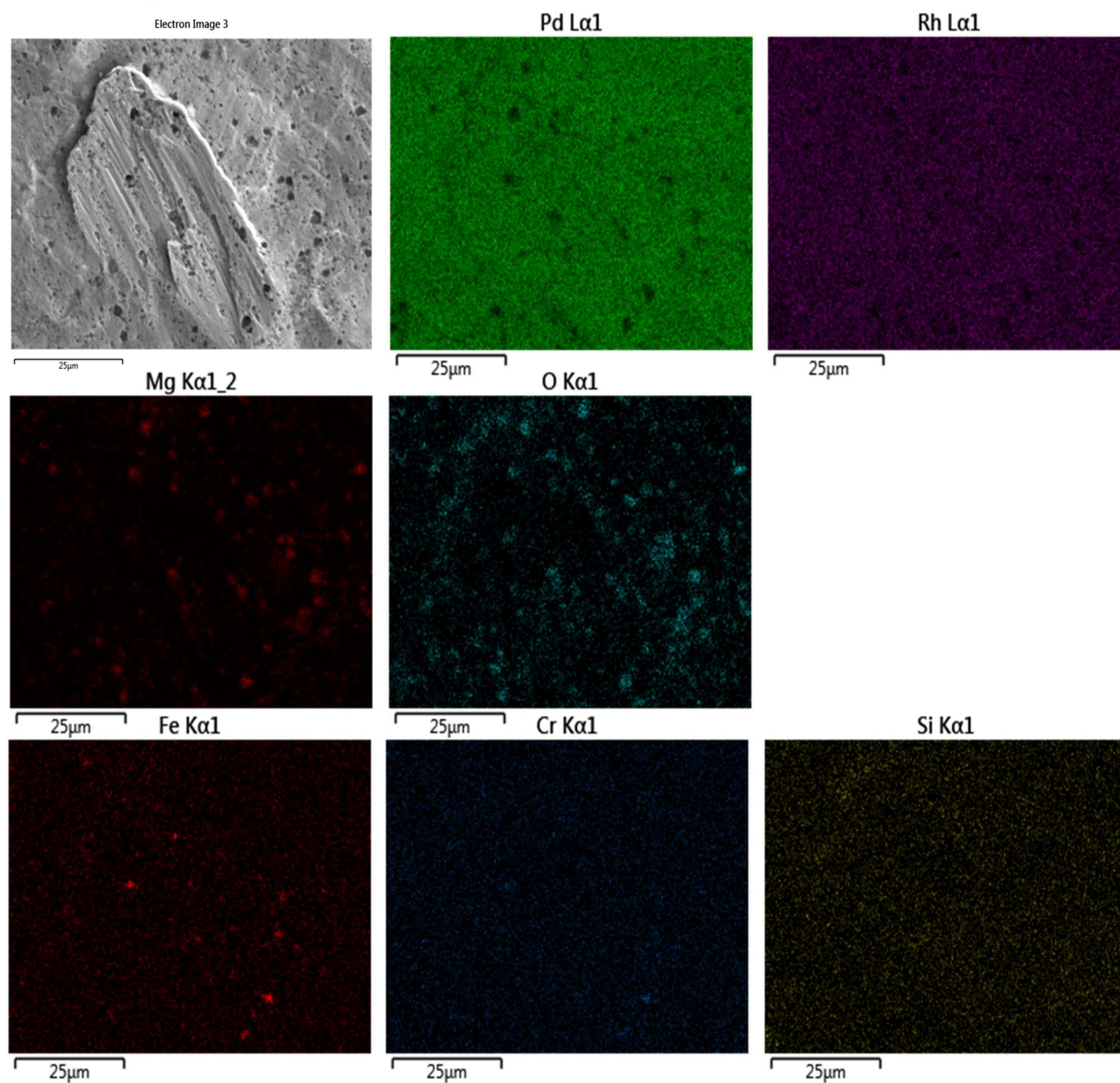
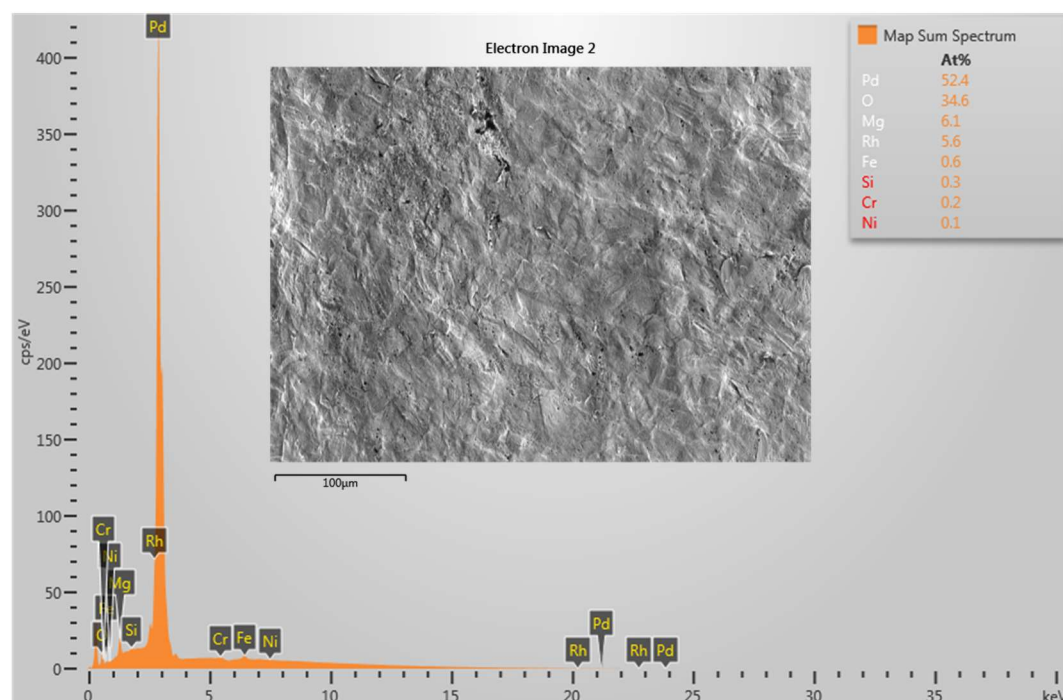


Figure 7. EDX spectrum from one region of the Pd-Rh foil.

Pd-Rh-Y Alloy SEM/EDX Analysis

SEM/EDX analysis of the Pd-Rh-Y foil revealed that the alloy was quite inhomogeneous. Referring to Figure 8, Pd- and Rh-poor regions can be seen, along with Y-rich regions. Also shown is the map for the P K α 1 peak, but this peak is nearly identical energetically as the Y L α 1 peak, and is probably mis-identified by the EDX software due to overlap. There is a strong correlation of the O signal to the Y signal, indicating the likely presence of a Y oxide. (The XRD spectrum above (Fig. 3) confirmed this as Y₂O₃.) The Fe and Cr signals are probably trace contamination from the SS foils used to roll out the alloy, as noted with the Pd-10%Rh foil. The SEM photograph shows a ‘dark’ region, whose SEM/EDX results are shown in Figure 9. The Pd, Rh, and Y maps for that image do not show any significantly different characteristics, therefore it can be concluded that the dark appearance is likely due to surface roughness and not compositional differences. Figures 10 and 11 are SEM/EDX results for Y-poor and Y-rich regions of the foil, respectively. The large difference in Pd:Y ratios confirms the foil’s inhomogeneity.

An attempt was made to re-melt this alloy in order to improve homogeneity, but the resulting button clearly showed that the alloy pieces (from the isotherm sample) had not fully melted and incorporated into the remainder of the material. No further work was done on this sample.

Figure 8. SEM/EDX analysis of region of Pd-Rh-Y foil (SEM photograph area). Elemental maps of Pd, Rh, Y, 'P', O, Fe, and Cr shown. EDX spectrum shown.

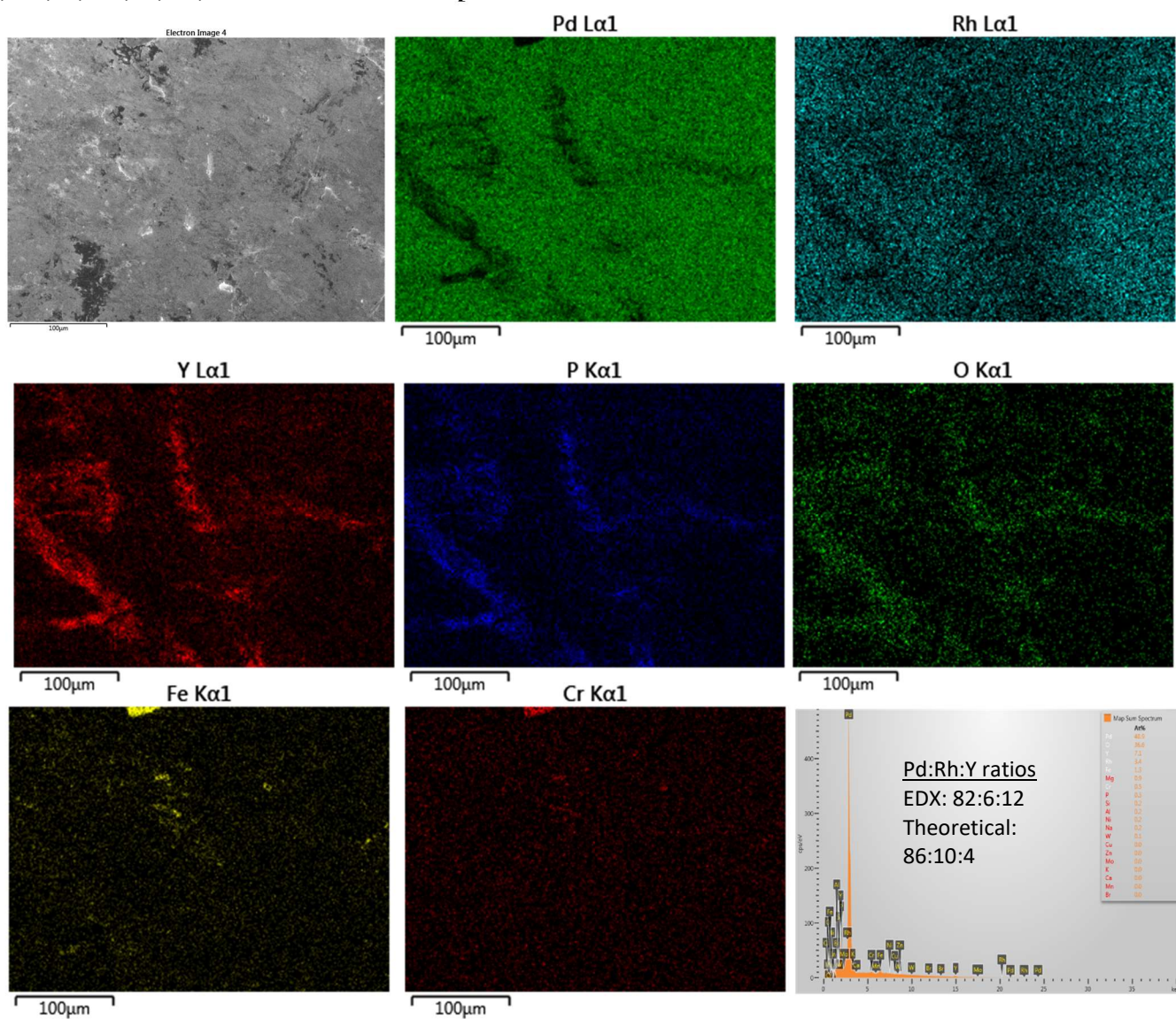


Figure 9. SEM/EDX analysis of ‘dark’ region of Pd-Rh-Y foil (box in SEM photograph). Elemental maps of Pd, Rh, and Y shown.

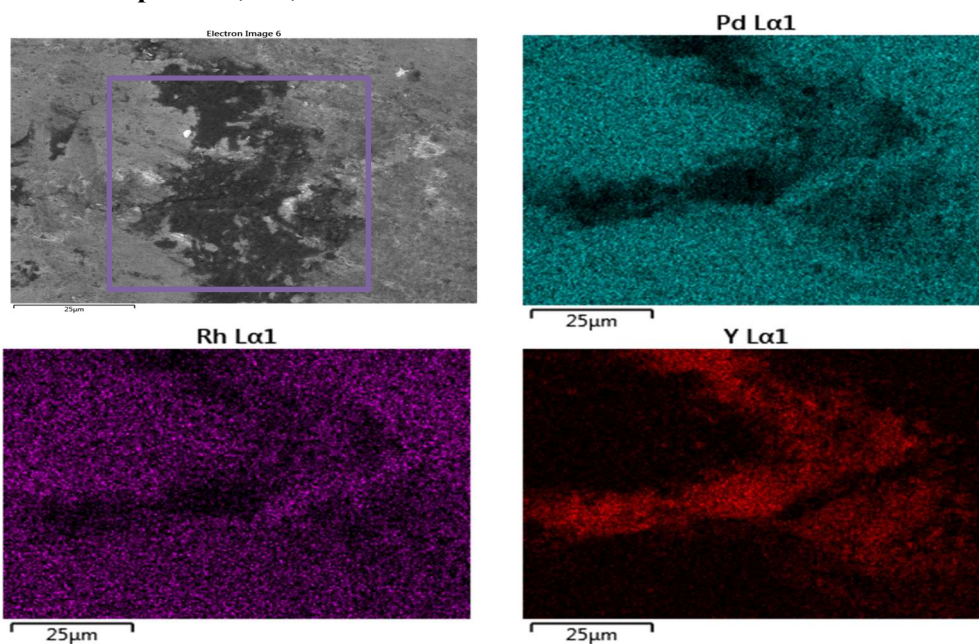


Figure 10. SEM/EDX analysis of low Y concentration region of Pd-Rh-Y foil (SEM photograph area). Elemental maps of Pd, Rh, Y, O, Fe, and Cr shown. EDX spectrum shown.

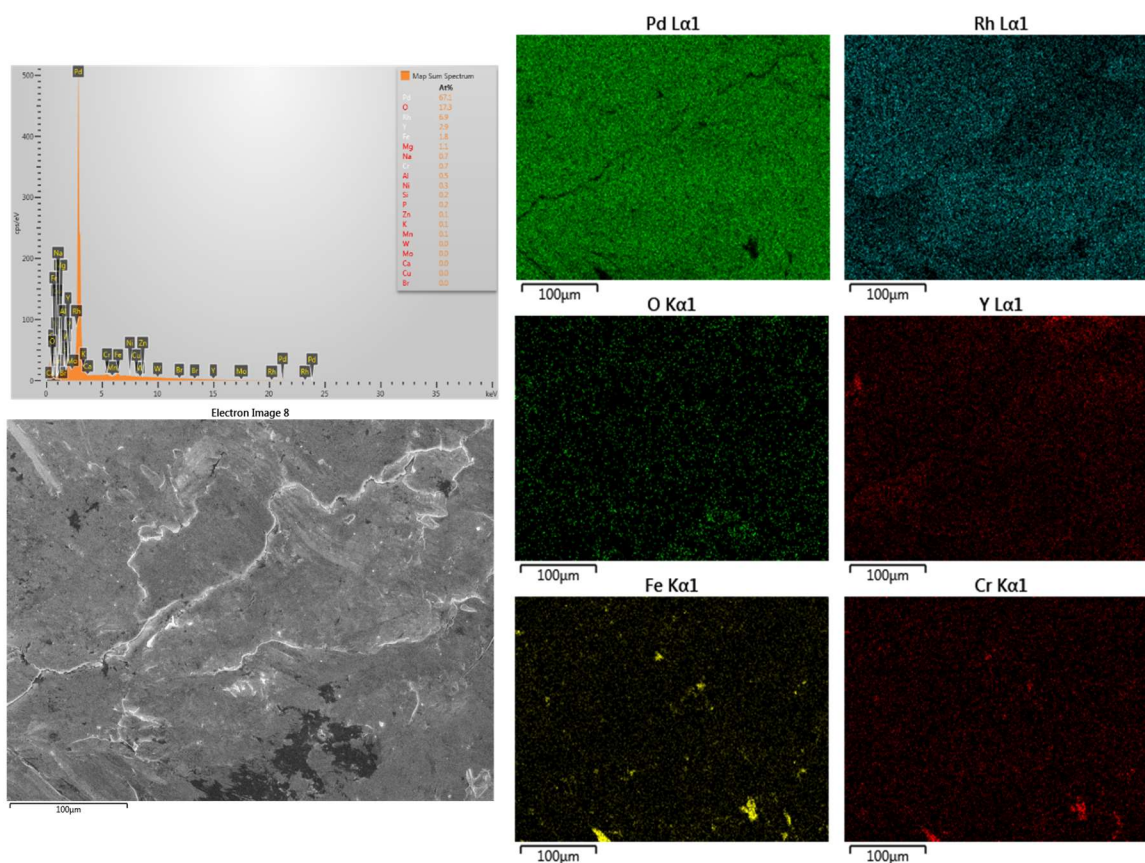
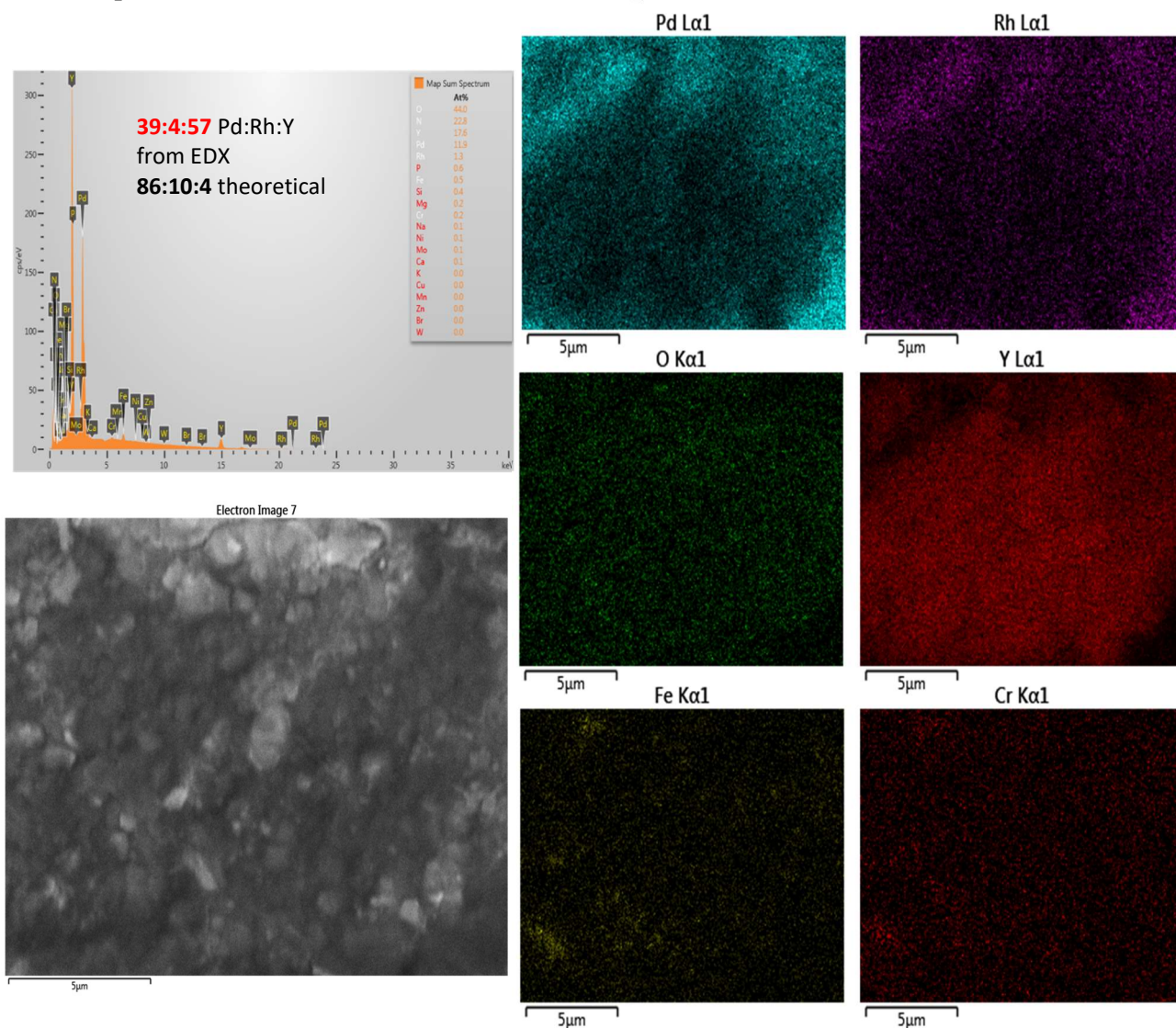


Figure 11. SEM/EDX analysis of high Y concentration region of Pd-Rh-Y foil (SEM photograph area). Elemental maps of Pd, Rh, Y, O, Fe, and Cr shown. EDX spectrum shown.



Pd-Au-Y Alloy SEM/EDX Analysis

Figures 12, 13, and 14 show SEM images and the corresponding EDX spectrum and elemental maps of 3 regions of the Pd-Au-Y alloy, which has nominal composition of $\text{Pd}_{0.84}\text{Au}_{0.15}\text{Y}_{0.01}$. The elemental maps seem to indicate some inhomogeneity in element distributions, as well as a small O content. The XRD spectrum (Figure 3) also showed a slight Y_2O_3 content.

Figure 12. SEM image, EDX spectrum, and Pd, Au, Y, and O elemental maps of a selected region of the Pd-Au-Y alloy foil.

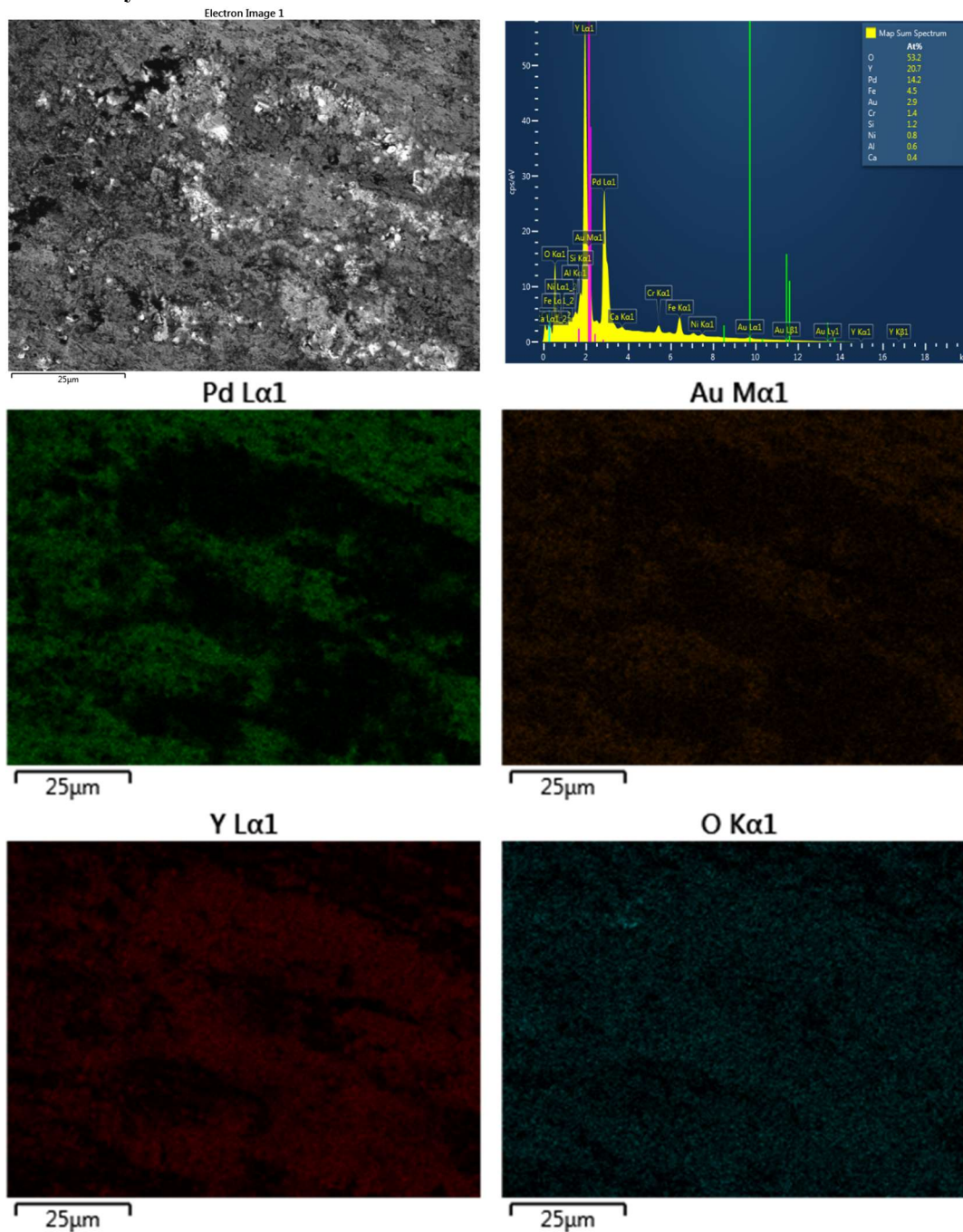


Figure 13. SEM image, EDX spectrum, and Pd, Au, Y, and O elemental maps of a selected region of the Pd-Au-Y alloy foil.

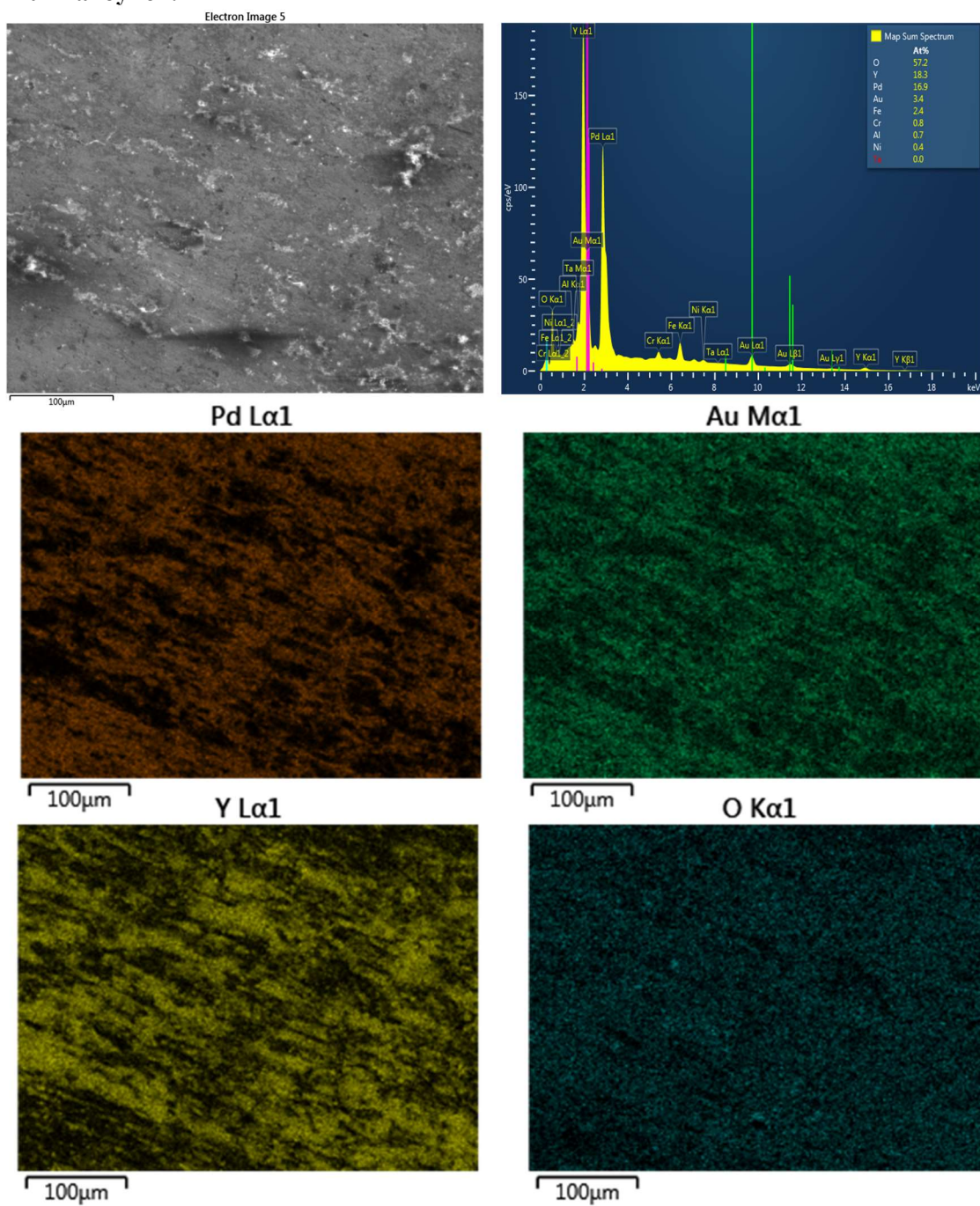
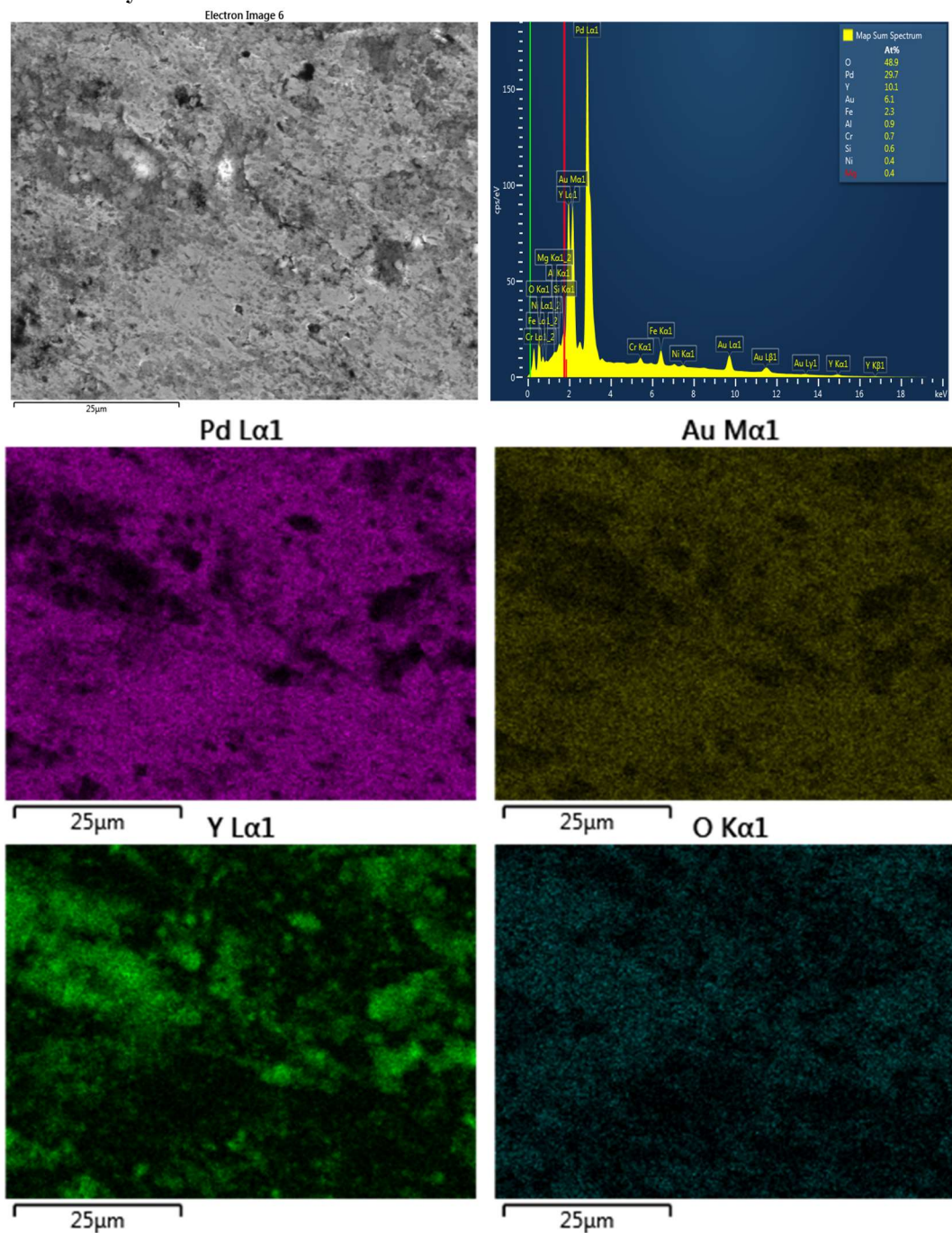


Figure 14. SEM image, EDX spectrum, and Pd, Au, Y, and O elemental maps of a selected region of the Pd-Au-Y alloy foil.

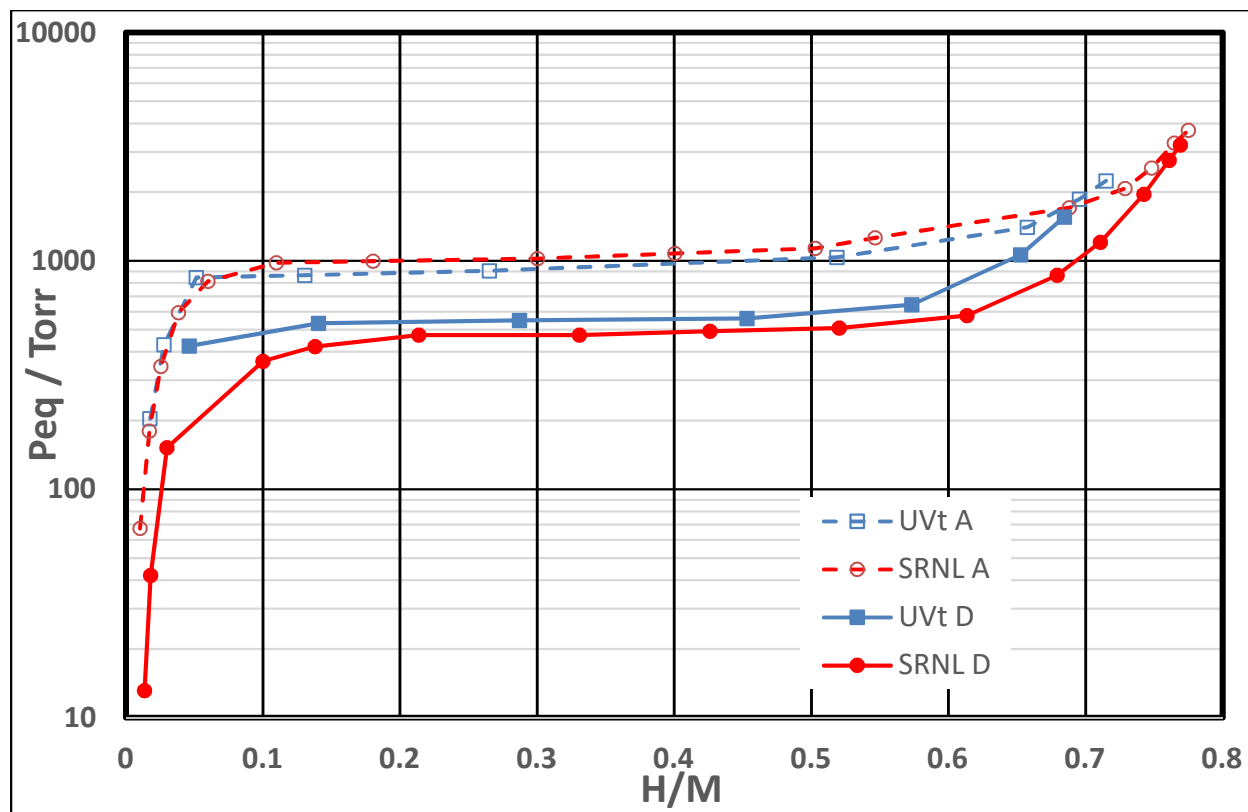


Figure

Pd-10% Rh Hydrogen Isotherms

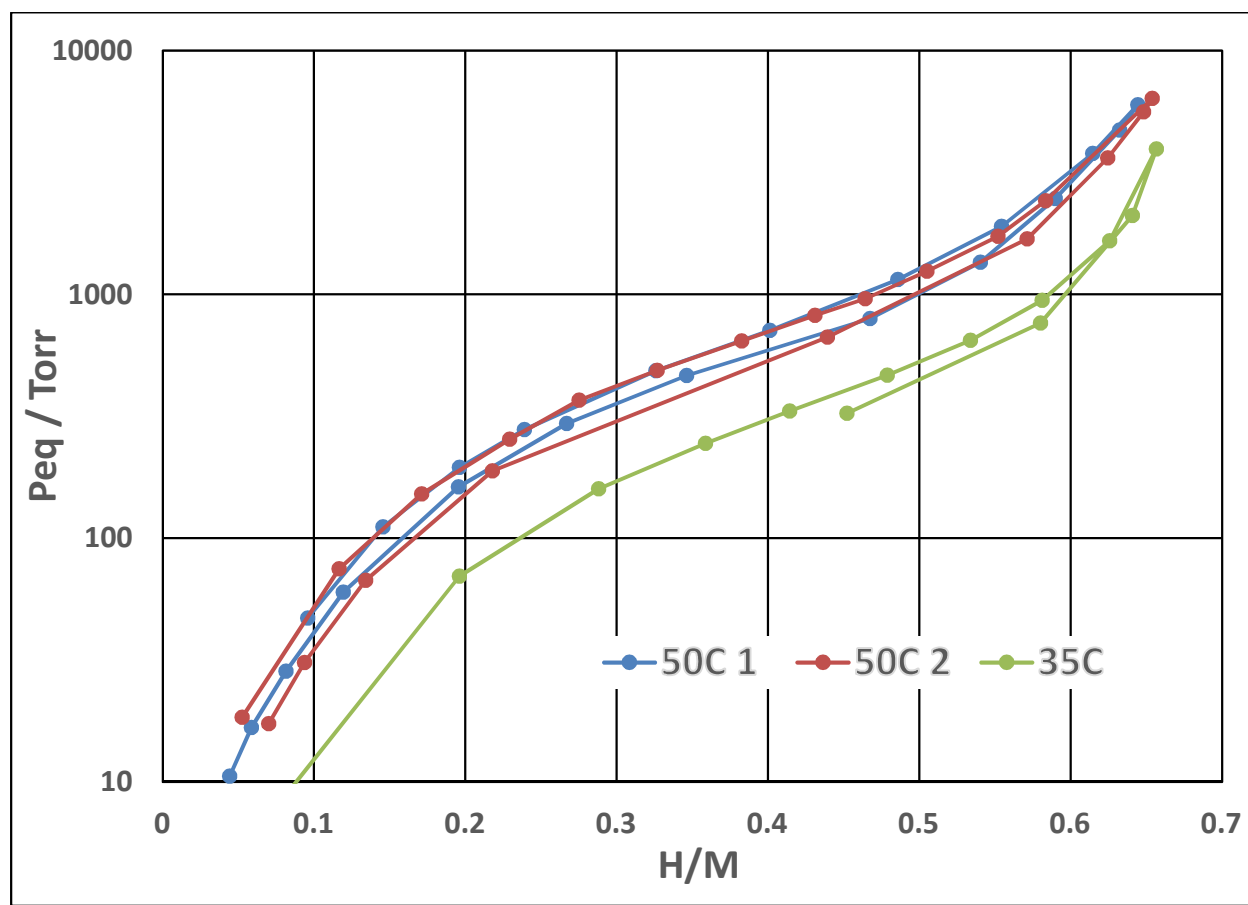
Figure 15 shows the 50 °C hydrogen absorption/desorption isotherm obtained from the SRNL 10%Rh-Pd foil, compared to a 50 °C isotherm obtained by T. Flanagan⁸ on a foil of similar composition prepared at the U. Vermont via arc melting. The differences noted can be attributed to the differences in preparation method and possible slight composition differences. Overall, this Figure demonstrates that the alloy made at SRNL is directly comparable to those made by the experts at the U. Vermont. The plateau flatness and the maximum capacity (H/M) indicate a well-annealed alloy. The imperfect matching of plateaux pressure may indicate a slight difference in (a) composition, (b) isotherm temperature, and/or (c) differences due to annealing or lack thereof.

Figure 15. 50°C Hydrogen Absorption/Desorption Isotherms. (Red – SRNL foil, Blue – U. Vermont (Ted Flanagan, UVt). Dashed - Absorption (A), Solid - Desorption (D).)



Pd-Rh-Y Hydrogen Isotherms

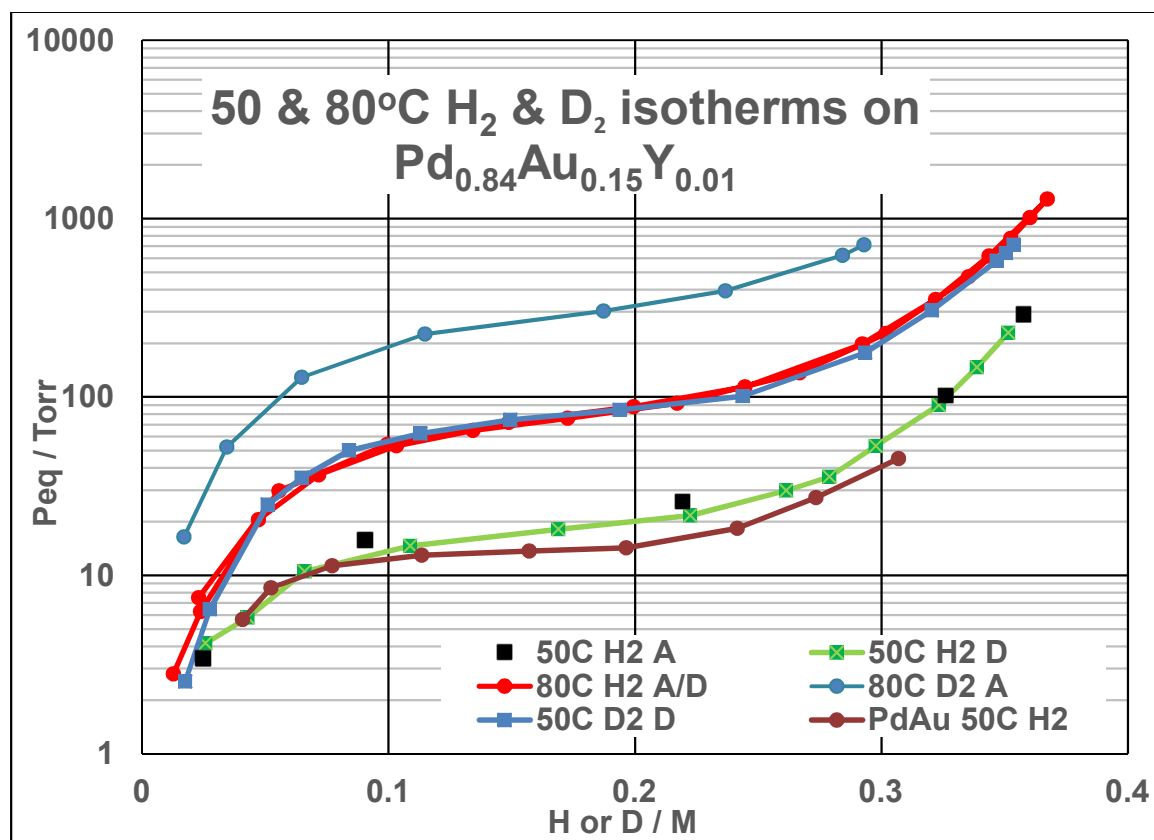
Figure 16 shows hydrogen isotherms obtained at 35 and 50 °C (replicate run at 50 °C) on the initial Pd-Rh-Y alloy foil, shown above to have significant chemical inhomogeneity due to Y oxidation. Chemical inhomogeneity invariably produces sloping plateaux or even no plateaux in isotherms, and these results display that problem. However duplicate isotherms at 50 °C indicate good reproducibility of the isotherms. Y is known to frequently form disordered alloys and that may be another reason for the heterogeneity evidenced by the highly sloped isotherms. Additional work is required to clarify the source.

Figure 16. Hydrogen Isotherms at 35 and 50 °C from SRNL Pd-Rh-Y alloy foil

Pd-Au-Y Hydrogen Isotherms

Figure 17 shows the protium (H_2) 50 and 80 °C absorption and desorption isotherms and 80 °C absorption and 50 °C desorption isotherms deuterium (D_2) isotherms obtained from the Pd-Au-Y alloy. (Note that the 50 °C D_2 desorption isotherm almost perfectly overlays the 80 °C H_2 isotherms.) Also shown for comparison is a published⁹ 50°C protium desorption isotherm from a Pd-15%Au alloy. The plateau slopes for the Pd-Au-Y alloy are not as flat as for the Pd-Au alloy which could be due to multiple causes. Of note is the lack of hysteresis and strong isotope effect noted with the Pd-Au-Y alloy.

Figure 17. Protium (H₂) and Deuterium (D₂) isotherms on the Pd_{0.84}Au_{0.15}Y_{0.01} alloy. Also shown is a 50°C protium desorption isotherm taken from a literature report on Pd_{0.85}Au_{0.15} alloy for comparison. (Absorption (A), Desorption (D))



4.0 Conclusions

The goal of this project was to establish alloy synthesis capabilities at SRNL for the study of poisoning-resistant hydride materials primarily for use in hydrogen separation processes. It was determined that the most viable in the short term was to utilize an existing tube furnace.

Three alloys have been prepared to date by melting in MgO crucibles wrapped in Ta foil in the tube furnace. Two can be considered as successes, and one evidenced difficulties that primarily arose from allowing the alloying element Y to oxidize. However, even this ‘failure’ was a learning experience that resulted in a procedure change in the synthetic process. It can therefore be stated that the initial year of this project can be considered to be quite successful.

The first alloy prepared was chosen to replicate prior work done under contract by Prof. T. Flanagan of the Univ. of Vermont’s Dept. of Chemistry. Direct comparison to those results was highly favorable, which encouraged proceeding. The second alloy prepared was chosen to (a) advance to ternary alloys, which are not as well studied, and (b) test the use of Y, an element shown in the prior research to have beneficial characteristics for carbon monoxide poisoning resistance. The third alloy prepared replaced the rhodium with gold as gold has been shown in the literature to provide resistance to sulfur poisoning if present in at least 15 atomic%.

These alloys demonstrated that SRNL now has the capability to make Pd-alloys. Remaining tasks are to determine the impact/need for annealing, and to determine the effect of poisons.

5.0 Path Forward

Now that the synthetic method has been developed, a series of likely candidate alloys should be prepared that systematically vary composition in an attempt to maximize desirable characteristics. In order to test the alloys, hydrogen absorption isotherms should be measured on virgin materials at at least two temperatures and in duplicate at at least one temperature (as was done in Figure 17). Then the alloy should be exposed to a poison or a mixture of poisons. Following, the isotherm determinations should be repeated to observe if rates and capacities have changed.

5% CO and 50 ppm H₂S in nitrogen can be commercially purchased off-the-shelf and would be good candidates for initial testing. However, due to the persistent character of S, a separate manifold would need to be constructed to dose with H₂S to prevent the primary isotherm measurement manifold from developing adverse S contamination. CO is probably less of a problem, but it too could be dosed on the second manifold. Materials that showed poisoning resistance could then be made into a gasket for a Cajon™ VCR fitting and a permeability test conducted on it per the procedure used by Prof. Flanagan in his prior research for SRNL.

The aforementioned research by Prof. Flanagan utilized a technique called partial internal oxidation to produce surface layers that were resistant to poisoning. This was desired since the fully oxidized materials had developed mud-flat-type cracking, which would be unacceptable as a membrane. The partially oxidized materials were resistant to developing cracks all the way through the material. For this, oxidizing furnaces, which could likely be used for annealing as well, would need to be located and employed. Finally, after developing an appropriate material, membrane manufacturers would be contacted and used to develop actual commercial membrane variants using the new alloy(s).

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