Contract No:

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Year-End Report: Development of Poison Resistant Palladium Alloys for Hydrogen Processing

This project successfully established SRNL synthetic capabilities for palladium binary and ternary alloys. These alloys were composed of elements that were hoped to give the material resistance to the poisoning effects of common hydrogen permeability poisons such as carbon monoxide and sulfur. Several experimental and operational difficulties were encountered and overcome during the first year of this project. The method established uses melting in a tube furnace at ~1700 ^{o}C to alloy the elements, followed by flattening and rolling the metal into thin foils. These foils were then characterized by scanning electron microscopy with energy-dispersive x-ray analysis, x-ray diffraction, and hydrogen absorption/desorption isotherm measurements.

Awards and Recognition

N/A

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

LDRD-2019-00063
LDRD External Report

Development of Poison Resistant Palladium Alloys for Hydrogen Processing

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Subcontractor: N/A

Thrust Area: NS

Project Start Date: October 1, 2018

Abstract: This project successfully established SRNL synthetic capabilities for palladium binary and ternary alloys. These alloys were composed of elements that were hoped to give the material resistance to the poisoning effects of common hydrogen permeability poisons such as carbon monoxide and sulfur. Several experimental and operational difficulties were encountered and overcome during the first year of this project. The method established uses melting in a tube furnace at ~1700 °C to alloy the elements, followed by flattening and rolling the metal into thin foils. These foils were then characterized by scanning electron microscopy with energy-dispersive x-ray analysis, x-ray diffraction, and hydrogen absorption/desorption isotherm measurements.

FY2019 Objectives

- Establish synthetic capability and/or Identify external synthesis partner/subcontractor
- Synthesize representative alloys
- Characterize alloys

Introduction

The SRNL Defense Programs Technology (DPT) Section did not have facilities to form new alloys for investigation. Therefore, an LDRD Project was proposed and accepted to establish alloy synthesis capabilities for the purpose of preparing poison-resistant palladium alloys. Synthetic capability has been achieved. Three Pd alloys have been prepared and characterized.

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 benefit to hydrogen isotope processes at SRS. One aspect of this is poison resistance. Several gases or contaminants in gases can absorb on Pd-alloy materials and severely block 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 (H_2S) or rotten-egg gas. Exposing Pd alloys to either of these two compounds results in an almost complete blocking 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 H_2S) 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 adding any other alloying element does.

At SRS there are two primary uses of Pd and a Pd-Ag alloy: Pd supported on kieselguhr is the base component of the TCAP process used to separate hydrogen isotopes, and Pd-23at% Ag is the typical diffuser membrane material used to extract H isotopes from waste gas streams or from water-gas shift products. It would be advantageous to SRS (and other hydrogen purification process users) to have alloys that resist poisoning, as this allows for longer process lifetimes and the possibility of lower temperature operation (Pd-Ag membranes are typically operated at ~400°C to prevent CO poisoning and beta-phase formation).

Approach

After locating various potential synthetic facilities, both at SRNL and elsewhere, the most efficacious one was chosen. This turned out to be a melting process using a tube furnace located in SRNL (Figure 1). Synthetic capability was demonstrated initially by preparing a binary Pd-10% Rh alloy by melting a mixture of elements at ~1700°C in a tube furnace. The alloy was characterized with SEM/EDX, XRD, and hydrogen isotherm determinations, and compared to prior research results obtained on foils made elsewhere. The comparison was highly favorable and thus indicated proceeding was warranted.

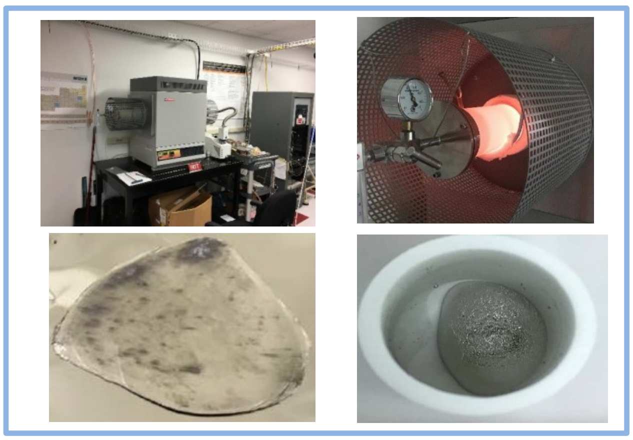


Figure 1. *Clockwise from upper left: Tube Furnace, Operating Tube, Pd-Rh Alloy button, Rolled Pd-Rh foil*

Subsequently, two ternary alloys were prepared, nominally $Pd_{0.86}Rh_{0.1}Y_{0.04}$ and $Pd_{0.84}Au_{0.15}Y_{0.01}$. In the first, the highly oxygen-reactive material Y was found to have picked up substantial oxygen, which formed an insoluble oxide. Procedural modification then solved this problem and the third ternary alloy was prepared. That alloy did still evidence a small oxide content. The choice of alloying elements was dictated by prior research in this area indicating Y offered CO-poisoning resistance and Au offered S-poisoning resistant if present in 15 at% or greater amount. The subsequent plan in following years was to expose these materials to the appropriate poisons and re-characterize their hydrogen isotherm characteristics to determine how much poison resistance had been conferred. Composition was to be optimized and possible other alloying elements tested to obtain maximized performance in membrane applications.

Results/Discussion

This project was initially proposed as a multi-year project. The primary objectives of the first year were to establish alloy synthesis capability and make and test several alloys. Three alloys were synthesized and characterized in FY19; $Pd_{0.9}Rh_{0.1}$, $Pd_{0.86}Rh_{0.1}Y_{0.04}$, and $Pd_{0.84}Au_{0.15}Y_{0.01}$. The first was simply to establish that the alloy synthesis process developed under this project produced alloys of acceptable quality. This was shown by comparing to ones prepared by a University of Vermont chemist, Prof. T. Flanagan, under a prior research contract with SRNL. Figure 2a shows the Pd-Rh alloy's XRD compared to a Pd-Rh-V alloy supplied by Prof. Flanagan. Figure 3 shows the Pd-10%Rh foil's EDX elemental maps which show no chemical inhomogeneity, i.e. the alloy was fully alloyed. Figure 4 compared the 50°C hydrogen isotherm with prior Flanagan results. The differences noted are well within normal experimental error for the synthetic process, and show the prepared alloy was of high quality.

The second alloy used a highly oxygen-reactive metal, yttrium (Y), and the synthetic procedure used did not adequately protect against this. Thus, the alloy was inhomogeneous and contained significant Y_2O_3. Subsequently, the procedure was altered, and the third alloy prepared. XRD results (Figure 2b) show the problem was mostly resolved with only a small oxide content being detected. Future research would include the use of a referential oxide getter in the melting furnace. Hydrogen isotherms (Figure 5) showed slightly sloping plateaux which typically indicates the need for the application of post-rolling annealing, which can also be done at SRNL.

Figure 2a. XRD spectra from Pd-10%Rh (black) and a Pd-Rh-V alloy (green)

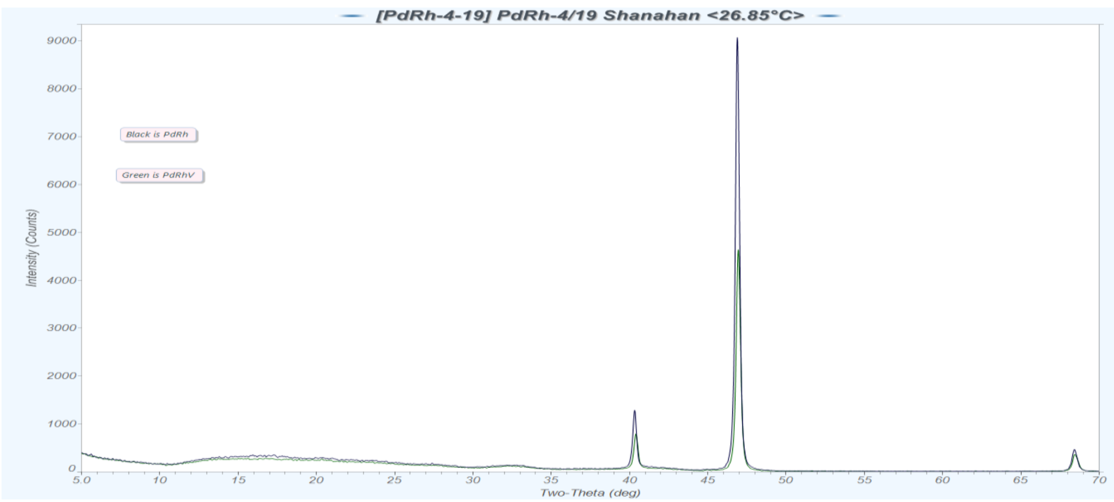


Figure 2b. XRD spectra from Pd-15%Au-1%Y alloy

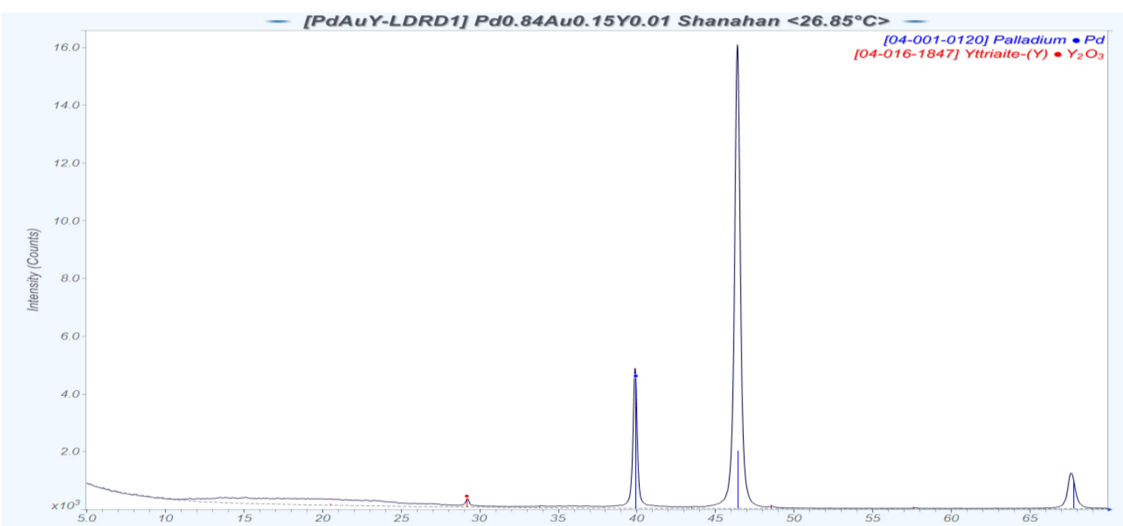


Figure 3. SEM/EDX analysis of indicated region of Pd—10%Rh foil (circled on low magnification SEM photograph of the whole foil piece, lower left). Elemental maps of Pd, Rh, Mg, and O shown. (MgO crucibles were used to prepare the alloys.)

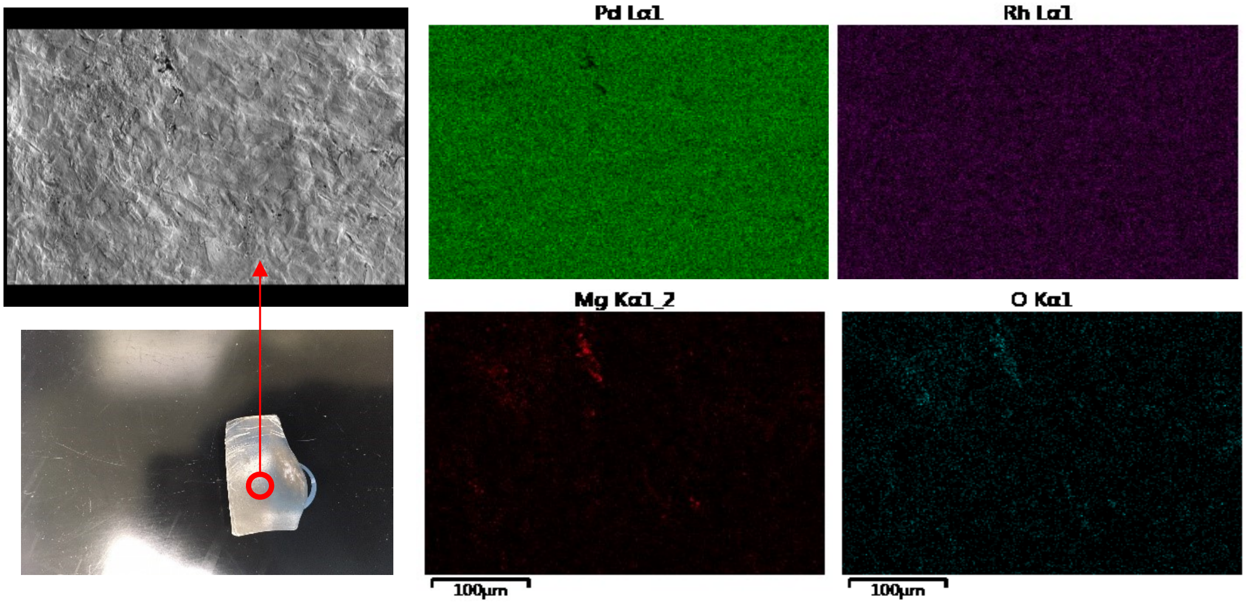


Figure 4. 50°C Hydrogen Absorption/Desorption Isotherms from Pd-10%Rh alloy (Equilibrium Pressure vs. Hydrogen-to-Metal ratio). (Red – SRNL foil, Blue – U. Vermont (Ted Flanagan, UVt). Dashed - Absorption (A), Solid - Desorption (D).)

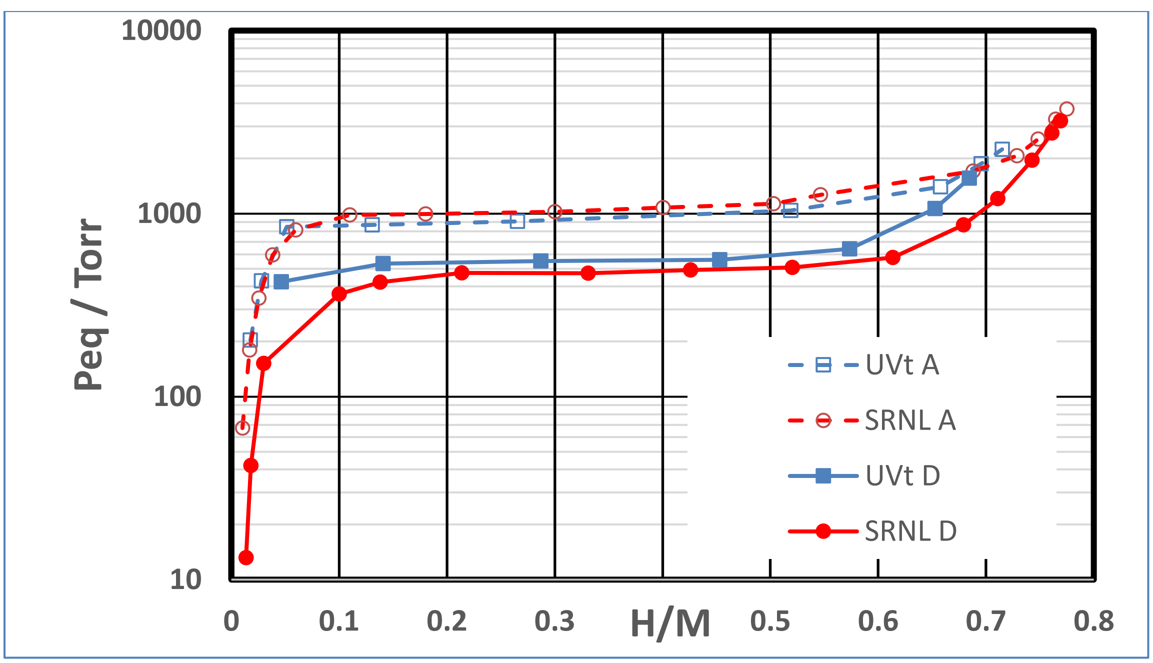
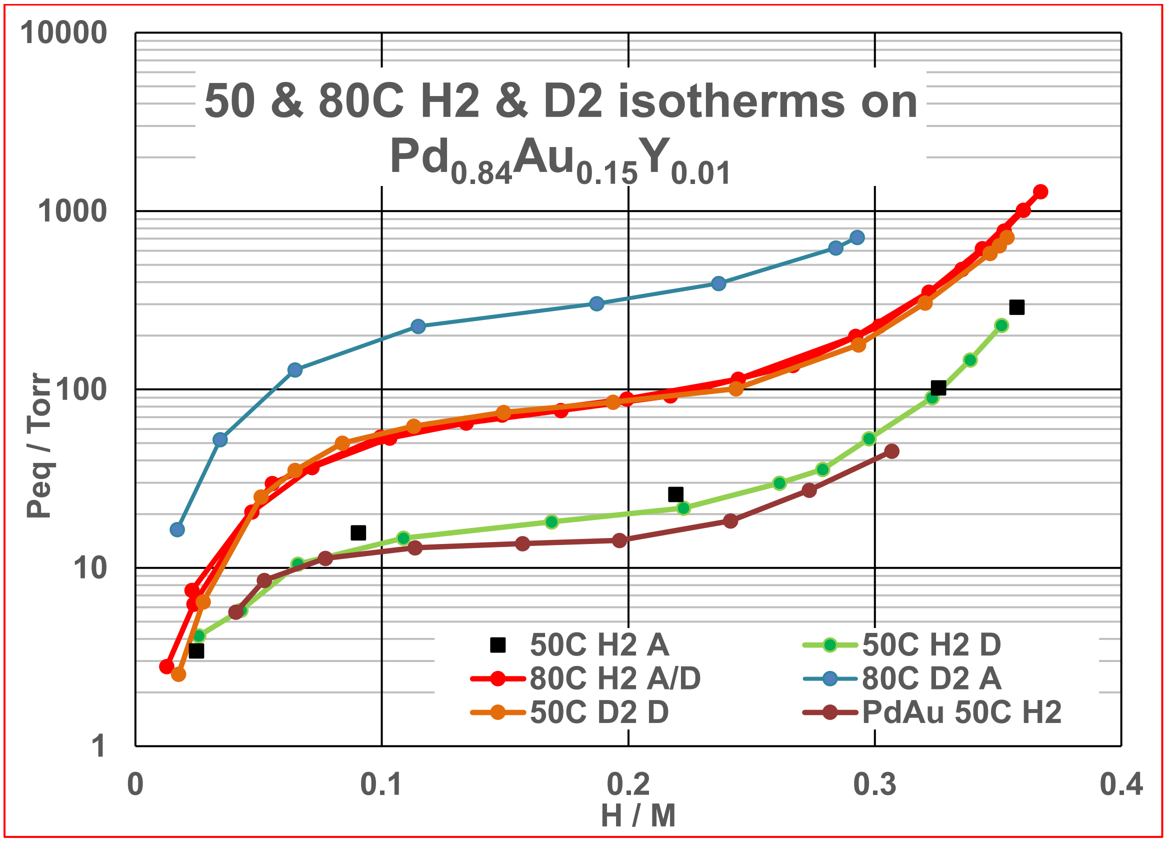


Figure 5. 50 and 80°C Hydrogen and Deuterium Absorption/Desorption Isotherms from Pd-15%Au-1%Y alloy (Equilibrium Pressure vs. Hydrogen-to-Metal ratio) compared to published Pd-15%Au (PdAu) alloy. (Absorption (A), Desorption (D).)



FY2019 Accomplishments

- Identified the most efficacious way to develop SRNL alloy synthesis capability
- Prepared and characterized three alloys and resolved synthetic issues

Future Directions

None. Funding was not continued.

If alternate funding can be obtained, alloys will be tested and optimized by standard statistically designed experiments.   Best performing materials will then be tested in a membrane simulation experimental apparatus.

FY 2019 Publications/Presentations

A report fully detailing the project results is in preparation.

If alternate funding can be obtained, the work is highly publishable, but more results are required. If a good poison-resistant alloy composition is found, it should be patentable.

References

None.

(Note: The prior research effort with T. Flanagan produced several journal publications which are not explicitly referenced here. Considerable literature from other sources exists as well.)

Acronyms

SEM – Scanning Electron Microscopy – shows microscopic physical characteristics
EDX – Energy Dispersive X-ray (analysis) – shows elemental composition and distribution
XRD – X-Ray Diffraction – shows degree of crystallinity

Intellectual Property

None.

Total Number of Post-Doctoral Researchers

None.

Total Number of Student Researchers

None.