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Material synthesis and hydrogen storage of palladium-rhodium alloy

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Material synthesis and hydrogen storage of palladium-rhodium alloy

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Abstract

Pd and Pd alloys are candidate material systems for Tr or H storage. We have actively engaged in material synthesis and studied the material science of hydrogen storage for Pd-Rh alloys. In collaboration with UC Davis, we successfully developed/optimized a supersonic gas atomization system, including its processing parameters, for Pd-Rh-based alloy powders. This optimized system and processing enable us to produce $\leq 50\text{-}\mu\text{m}$ powders with suitable metallurgical properties for H-storage R&D. In addition, we studied hydrogen absorption-desorption pressure-composition-temperature (PCT) behavior using these gas-atomized Pd-Rh alloy powders.

The study shows that the pressure-composition-temperature (PCT) behavior of Pd-Rh alloys is strongly influenced by its metallurgy. The plateau pressure, slope, and H/metal capacity are highly dependent on alloy composition and its chemical distribution.

For the gas-atomized Pd-10 wt% Rh, the absorption plateau pressure is relatively high and consistent. However, the absorption-desorption PCT exhibits a significant hysteresis loop that is not seen from the 30-nm nanopowders produced by chemical precipitation. In addition, we observed that the presence of hydrogen introduces strong lattice strain, plastic deformation, and dislocation networking that lead to material hardening, lattice distortions, and volume expansion.

The above observations suggest that the H-induced dislocation networking is responsible for the hysteresis loop seen in the current atomized Pd-10 wt% Rh powders. This conclusion is consistent with the hypothesis suggested by Flanagan and others (Ref 1) that plastic deformation or dislocations control the hysteresis loop.

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Contents

1	Introduction	10
2	Experimental procedures	12
2.1	Powder sample preparation	12
2.2	Material characterization	12
2.3	Material synthesis and processing	13
2.3.1	Principle of gas atomization.....	13
2.3.2	Feed stock material	15
2.3.3	Process development and optimization	17
2.3.4	Metallurgical property of Pd-10wt% Rh powders produced at UCD	20
2.4	Hydrogen storage science.....	28
2.4.1	Material	28
2.4.2	Hydrogen–metallurgy interaction	28
2.4.3	Vicker’s microhardness.....	39
2.4.4	Lattice strain and deformation by XRD	41
2.4.5	Hydrogen absorption-desorption behavior.....	43
3	Summary and discussion.....	46
3.1	Material synthesis and process optimization.....	46
3.2	Material science of H-storage.....	48
4	Conclusions.....	53
5	Future work.....	54

Figures

Figure 1.	Phase diagram of binary Pd-Rh system that shows the completely miscible Pd-10 wt% Rh alloy at $\geq 550\text{ }^{\circ}\text{C}$	11
Figure 2.	The isotherm absorption PCT curves measured by S. Guthrie.....	11
Figure 3.	The schematic illustrates the principle of gas atomization.....	14
Figure 4.	The plot shows the correlation among the measured secondary dendrite arm spacing (SDAS), measured powder diameter, and calculated cooling rate.....	15
Figure 5.	The digital image shows a typical shape and size of the recycled feedstock, consolidated by cold isostatic pressing (CIP).....	15
Figure 6.	The digital image shows the final configuration of the supersonic gas atomization constructed at UC Davis through SNL/UCD collaboration.	18
Figure 7.	SEM image showing the typical powder morphology of the current gas-atomized Pd-10 wt% Rh powders, $\leq 180\text{ }\mu\text{m}$	20

Figure 8. The SEM image shows the Pd-10 wt% Rh powders after being sifted to $\leq 53 \mu\text{m}$	21
Figure 9. Auger spectroscopy analysis shows the absence of foreign elements on the as-atomized powder surface.	23
Figure 10. Optical images of the glycerol etched powders show the well-defined dendrites in the large size powders (left) and equiaxed cells in the small size powders (right).	24
Figure 11. The SEM image and its corresponding Rh/Pd wt% ratio profile by WDS shows localized variation in alloy composition at dendrite boundaries. The marked line in the SEM image above is the location of the electron beam probe.	25
Figure 12. Typical microstructure in the large and small size powders and Rh composition profile across the dendrite/cell boundary.	26
Figure 13. Physical and chemical limits established from the standard deviation of Rh/Pd wt% calculated from the WDS analyses of more than thirty powders of various sizes.	27
Figure 14. PCT curves generated from the product lot #15 and the final UCI mix in 2000 by Meeker were reproducible.	27
Figure 15. SEM images at 2000x magnification show the effect of the H-cycling on the surface morphology.	29
Figure 16. 5-kV SEM images at magnification of 10,000x (left) and 50,000x (right) illustrate how the surface roughness changes with number of H-cycles.	30
Figure 17. FIB/SEM imaging is effective for mapping the strain field induced by lattice deformation related to atomic displacement, distortion, and mis-orientation.	32
Figure 18. FIB/SEM images show the 0.5- to 1- μm sized complex lattice strain contrast, induced by H-cycling, within each cell in the powders of all sizes.	33
Figure 19. FIB/TEM images show the lattice strain evolution induced by H-cycling for the 50- μm and 5- μm powders. The lattice contrast intensity increases as the number of H-cycles increases.	34
Figure 20. TEM/BF images of both 50- μm and 5- μm powders show the H-induced dense dislocation networking accompanied by strong lattice strain.	36
Figure 21. TEM/BF images at higher magnification show a greater detail of the dislocation networking, accompanied by strong lattice strain, as well as the Δd reduction upon H-cycling.	37
Figure 22. The enlarged TEM/BF images of the large size powder (50 μm) illustrate the areas selected for estimating the inter-dislocation spacing (Δd).	38
Figure 23. TEM/BF images show the surface roughness increasing with increasing number of H-cycles (left column). The enlarged images in the right column demonstrate the correspondence between the extruded steps and the slip line underneath for the 50- μm powders subjected to 8 H-cycles. The upper inserts are SEM images of the 50- μm powder surface with 1 and 8 H-cycles.	39
Figure 24. The SEM images illustrate decreasing Vicker's indent size for the powders from the 800 °C annealed, as-atomized, 1 H-cycle, and 8 H-cycle powders.	40

Figure 25. The plot illustrates that the Vicker's microhardness increases with increasing number of H-cycling for both 10- and 25-gram loads.....	41
Figure 26. Progressive XRD peak broadening observed from the powder sample with 800 °C/2minutes annealing (top), as atomized (2 nd), 1-H cycle (3 rd), and 8-H cycle (bottom).....	42
Figure 27. XRD peak broadening increases with the number of H-cycles.....	43
Figure 28. PCT curves generated from the three different groups in SNL/CA. Upper left by D. Meeker in 2000 using the custom designed manual operation; upper right by K. Gross in 2001 using a customer-designed fully computer-automated operation; lower by M. Ong in 2010 using the existing commercially available system.	44
Figure 29. The PCT curve for the powders subjected to 8 H-cycles.	45
Figure 30. The overall design, construction, and system performance of the helium gas atomization system constructed at UC Davis, through the SNL/CA–UC Davis collaboration.	47
Figure 31. Comparison of PCT curves between 1 H-cycle and 8 H-cycles shows minimal changes in hysteresis loop shape and size.	49
Figure 32. SEM images show H-induced powder surface roughening. (a) The large-powder surface contains slip bands and (b) the small size-powder surface contains scallop-like distortions.	49
Figure 33. The experimental data composite illustrates the H-induced metallurgical evolution and its implication to PCT behavior, hysteresis loop in particular.	50
Figure 34. Comparison of metallurgy and PCT behavior between the 50- μ m gas-atomized powders with chemically precipitated 30-nm nanopowders. The PCT result and TEM/BF images of the nanopowders were generated by M. Ong, D. Robinson, and B. Jacobs (Ref. 8).	51

Tables

Table 1. Impurity by ICP (wppm).....	16
Table 2. Acceptable impurity (wppm).	16
Table 3. Automated process parameters recording.	19
Table 4. Typical production yield.	19
Table 5. The impurity concentration of the UCI mix powders.	22
Table 6. He concentration (atomic ppm).....	23
Table 7. Vicker's microhardness by Vicker's diamond indentation.....	41
Table 8. Peak broadening calculated from the XRD spectra in Figure 26.....	42

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1 Introduction

Hydrogen is an emerging alternative energy source for both transportation and defense-related applications. Palladium (Pd-), magnesium (Mg-), and sodium-aluminum (Na-Al-) alloys are promising candidate materials for H-storage. Palladium-rhodium (Pd-Rh) alloy is an especially interesting candidate due to its good miscibility (Fig. 1), thermal stability, and high PCT pressure and capacity (Fig. 2). To advance H-storage technology and system performance, the interaction of H with the storage alloy medium, Pd-Rh-based alloy, must be understood.

In the 1990s, Guthrie and Yang studied the isotherm PCT behavior for the gas-atomized Pd-Rh-based alloys made by Engelhard, Inc. The study showed that the absorption PCT curve is highly dependent on the metallurgical properties of the powders, and the absorption H-pressure plateau increases with Rh concentration (Fig. 2, left). We also found an inclined slope hydrogen plateau pressure from the submicrometer powders with non-uniform alloy composition, which was produced by chemical precipitation (Fig. 2, right). In addition, we encountered inconsistent material shipments with respect to quality and metallurgical properties of the powders supplied by the commercial vendor.

The related needs of sound H-storage science and consistent qualified material supplies led to the DOE's project for material synthesis and hydrogen science research and development (R&D) for Pd-based materials. Sandia National Laboratories/CA (SNL/CA) was tasked to develop and optimize a gas atomization process for controlling the metallurgy and understanding the science of H-storage of Pd-Rh alloys. For material synthesis and processing, we collaborated with Professor E. Lavernia of UC Davis (formerly at UC Irvine) to develop gas atomization of Pd-Rh-based alloys (Ref. 2-5). For H-storage science, we focused on establishing a correlation of processing, metallurgy and PCT isotherm behavior.

In this report, we present and discuss the scientific activities and experimental results and findings in both material processing and H-storage science.

Figure 1. Phase diagram of binary Pd-Rh system that shows the completely miscible Pd-10 wt% Rh alloy at $\geq 550^\circ\text{C}$.

Figure 2. The isotherm absorption PCT curves measured by S. Guthrie.

Left: absorption plateau pressure increases with wt% of Rh.

Right: a steep slope of absorption plateau pressure seen from the submicrometer Pd-5 wt% Rh powders produced by the chemical precipitation process.

2 Experimental procedures

2.1 Powder sample preparation

The powder samples required for the microstructure, chemical composition, and elemental segregation examinations were prepared using conventional metallographic mounting, slicing, polishing, and etching. The thin film samples for trans electron microscopy (TEM) imaging were prepared using the focused ion beam (FIB) technique. The instrument used was a FEI dual platform Helios NanoLab 600 FIB. TEM thin films were achieved by following the established manufacturing procedure using the FEI AutoTEM G2 software and a 30-kV Ga beam. The final thinning was completed manually using a 100-pA 30-kV Ga beam to remove the FIB-induced surface artifacts and/or surface damage.

2.2 Material characterization

Microstructure and surface morphology

The microstructure was examined using a combination of advanced electron optical imaging techniques. The techniques include optical metallography, scanning electron microscopy (SEM), dual beam FIB with SEM, and TEM with bright field (BF) imaging. SEM and TEM analysis were performed using a JEOL 7600 at 15 kV and CM30 at 300 kV, respectively. The solidification structure was obtained through optical imaging of a chemically etched cross section using a glycerol solution consisting of 50 mL of glycerol, 30 mL HCl, and 20 mL HNO₃.

Chemical composition

The bulk chemical composition of the powders was analyzed using a destructive glow discharge mass spectroscopy (GDMS) technique. The chemical uniformity and local elemental segregation of Pd and Rh across the powder diameter was measured by non-destructive electron probe microanalysis (EPMA) with wavelength dispersive *x*-ray spectroscopy (WDS). The EPMA/WDS analyses were conducted using a JEOL 8200 Superprobe at 15 kV.

Surface chemical composition

The chemical composition on the surface was analyzed by Auger electron spectroscopy using Physical Electronics Model 680 at 5.0 keV.

He concentration

The He concentration of the powders was analyzed by isotope dilution mass spectroscopy at Pacific Northwest National Laboratory (PNNL) in Washington.

Vicker's microhardness

The hardness was measured using Vicker's diamond indentation technique. The measurements were performed on metallographic polished powder cross sections.

Crystal lattice evolution

We used SEM and TEM imaging to qualitatively reveal lattice strain and used *x*-ray diffraction (XRD) peak broadening to assess relative lattice strain induced by the H-cycling.

SEM/TEM imaging is an effective technique to show the strain field contrast, and XRD peak broadening is effective for measuring lattice displacement, deformation, and atomic displacement and/or distortion. In the current study, we use this peak broadening technique to determine the relative lattice displacement or distortion induced by H-cycling. The peak broadening is expressed by ratio of full-width half-maximum (FWHM) of the low-angle peaks (111), (200), (220), and (222) of the Pd-Rh powders divided by FWHM of the 100% random powder XRD standard.

Isotherm H PCT measurements

The PCT behavior was examined on three different occasions between FY2000 and FY2010. The instrument used in FY2000 was manually operated, and in FY2001 it was a fully computer automated operation. The two systems were custom designed and built in-house at SNL/CA. These two custom built PCT systems have since been dismantled. Therefore, the descriptions of the systems are irrelevant and are not given here. The PCT system used in the FY2010 is the existing commercial system that is still in operation; the system hardware and its operation is described as follows:

The hydrogen absorption measurements were performed using a Micromeritics ASAP 2020. The hydrogen gas temperatures were 298 K for hydrogen absorption/desorption experiments. Prior to analysis, samples were degassed at 323 K under vacuum for 15 hours. In between each hydrogen absorption measurement, the sample was evacuated at room temperature for at least 60 minutes to remove as much hydrogen as possible.

2.3 Material synthesis and processing

2.3.1 Principle of gas atomization

The atomization processing in general consists of three key components: molten liquid metal of the target composition, gas atomizer to produce liquid droplets, and liquid metal solidification (Fig. 3).

Figure 3. The schematic illustrates the principle of gas atomization.

The cooling rate during gas atomization and solidification determines metallurgical properties such as microstructure morphology and size as well as chemical uniformity. In general, a slow cooling of large size powder results in a coarse dendrite with non-uniform alloy composition, attributed to elemental segregation to dendrite boundaries. The variation in cooling rate with powder diameter can be estimated based on the empirical relationship between secondary dendrite arm spacing (SDAS) and cooling rate.

$$SDAS = a\dot{T}^{-b}$$

where SDAS is secondary dendrite arm spacing, $\dot{T}$ is cooling rate, and a and b are constants related to the physical and solidification properties. The constants a and b for Pd-Rh alloys are found to be 6194.8 and 0.6484, respectively.

Figure 4 below illustrates the correlation among the calculated cooling rate, measured SDAS, and powder diameter in the gas-atomized Pd-Rh powders during solidification.

Figure 4. The plot shows the correlation among the measured secondary dendrite arm spacing (SDAS), measured powder diameter, and calculated cooling rate.

2.3.2 Feed stock material

The initial feedstock used was the Pd-10 wt% Rh drop shot droplets, fabricated by Johnson & Matthey, Inc. in Pennsylvania. The drop shot droplet size is 0.25 – 0.5" in diameter, suitable for induction melting. For the recycled feedstock, we used the ~1/2" nodules, by cold isostatic pressing (CIP) of oversized powders at UC Davis (UCD) (Fig. 5). The alloy composition of the initial drop shot droplets is Pd 89.53 wt% Rh, 10.39 wt% analyzed by inductively coupled plasma (ICP) wet chemical analysis.

The elemental impurity composition by GDMS is shown in Table 1. The impurity level meets the impurity level expected as shown in Table 2.

Figure 5. The digital image shows a typical shape and size of the recycled feedstock, consolidated by cold isostatic pressing (CIP).

Table 1. Impurity by ICP (wppm).

Li	0.02	Pd	Matrix
Be	< 0.005	Ag	1.4
B	3.0	Cd	< 0.1
C	< 0.1	In	0.02
N	< 0.5	Sn	0.09
O	< 5	Sb	1.1
F	< 0.01	Te	0.39
Na	0.05	I	< 0.05
Mg	2.2	Cs	< 0.001
Al	1.1	Ba	0.003
Si	52	La	0.009
P	0.05	Ce	< 0.1
S	0.10	Pr	< 0.1
Cl	< 0.01	Nd	0.05
K	< 0.01	Sm	0.01
Ca	3.1	Eu	< 0.005
Sc	< 0.001	Gd	< 0.005
Ti	1.2	Yb	0.008
V	0.02	Dy	< 0.005
Cr	3.0	Ho	< 0.005
Mn	0.75	Er	< 0.005
Fe	15	Tm	< 0.005
Co	0.07	Yb	< 0.005
Ni	0.68	Lu	< 0.005
Cu	28	Hf	0.03
Zn	0.65	Ta	< 0.5
Ga	< 0.005	W	0.26
Ge	< 0.05	Re	< 0.01
As	0.14	Os	< 0.005
Se	0.54	Ir	5.1
Br	< 0.01	Pt	270
Rb	< 0.005	Au	1.5
Sr	0.01	Hg	< 0.05
Y	< 0.005	Tl	< 0.01
Zr	0.98	Pb	1.6
Nb	0.05	Bi	< 0.05
Mo	0.19	Th	< 0.01
Ru	32	U	0.018
Rh	Matrix		

Table 2. Acceptable impurity (wppm).

<u>Acceptance criteria</u>	
<u>Element</u>	<u>WPPM</u>
Ag	<100
Al	<200
As	<100
Au	<100
B	<200
Ca	<100
Cr	<100
Cu	<100
Fe	<100
Ir	<100
K	<100
Mg	<100
Mn	<100
Na	<100
Pt	<500
Si	<100
Sn	<100
Ti	<100
Zn	<100
Zr	<100
Total impurity less than 1000 wppm.	

2.3.3 Process development and optimization

Design factors

Based on the above scientific principles, we developed and optimized a fast-cooling supersonic gas atomization system that took into consideration the following design factors:

- Crucible material and capacity capable of holding the maximum achievable superheating temperature: $\sim 150\text{--}200\text{ }^{\circ}\text{C}$ and holding kilogram-range liquid metal.
- A nozzle that maintained the temperature of the molten liquid metal prior to entering the atomizer
- Molten liquid exit configuration
- Designed He gas atomizer with 18-hole outlet for controlling the liquid metal droplets' size and cooling rate.
- Chamber height extension for ensuring a complete solidification before the powders reached the powder collection pool.
- Cyclone separator for collecting the powders smaller than $10\text{ }\mu\text{m}$ for environmental consideration.
- Fully automated computer hardware and software control for remote operation, data analysis, and archival purposes.

The final configuration of the gas atomization system was constructed based on extensive atomization test runs (as shown in Fig. 6) performed in 2006. This atomization system achieves the following design criteria and objectives:

- Established the optimum hardware design, processing parameters, and their conditions for improving production capacity, yield and cooling rate (Table 3). The ultimate system is able to increase production capacity, yield, and cooling rate to 3–4 kg, 45% for $\geq 50\text{-}\mu\text{m}$ powders, and $2 \times 10^5\text{ K/sec}$, respectively. The typical production yield and the powder size distribution are demonstrated in Table 4. Due to economic considerations, it would be desirable to improve the production yield further to $>>50\%$.
- The Pd-10 wt% Rh powder production is reproducible and meets the material property requirements—PCT and impurity level in particular—for SNL mission-driven applications (Fig. 7 and Table 5).
- The system is fully computer automated for controlling remote operation and data archiving.
- Using this gas atomization system, we produced about 14 kilograms Pd-10 wt% Rh powders, $10\text{--}50\text{ }\mu\text{m}$, for the R&D activities.
- This fast-cooling gas atomization technology was established in late 2000.

Figure 6. The digital image shows the final configuration of the supersonic gas atomization constructed at UC Davis through SNL/UCD collaboration.

Table 3. Automated process parameters recording.

Experimental Data Log
Sandia Powder Production Facility

Experiment # Date:

Researcher:

Crucible Used: Atomization Nozzle:

Alloy System: Charge Weight: Grams

Lot #: Manufacturer:

Physical Characteristics: ☒ Pre-alloyed

Pouring Tube
Material:

Diameter: inch

Profile: inch

Backfill
Gas:

Chamber Pressure: psi

Vacuum Reading: in. Hg

Atomization
Gas:

Dynamic Pressure: psi

Initial Supply Pressure: psi

Final Supply Pressure: psi

Heat Start: Thermocouple Discrepancy: C

Hold Time: Pour Temperature: C

Pour Time: Approx Height of Molten Metal in Crucible: inches

Atomization Time: seconds ☒ Successful

Comments:

Table 4. Typical production yield.

Experiment #39

Starting material	1645.5
Remaning in crucible	108.8
Total Sprayed Material	1536.7
$x > 180 \mu m$	385.9
$180 \mu m > x > 53 \mu m$	601.7
$x < 53 \mu m$	668.2
Loss	-119.1
Total $< 180 \mu m$	1269.9
% $< 53 \mu m$ under $180 \mu m$	52.6%
% sprayed material $< 180 \mu m$	82.6%
% sprayed material $< 53 \mu m$	43.5%

2.3.4 Metallurgical property of Pd-10wt% Rh powders produced at UCD

Powder morphology

The Pd-based alloy powders produced from the above gas atomization system contain the powders between 10 and 180 μm in diameter. The powders then can be sifted to achieve the size of interest. The SEM image in Figure 7 shows the overall powder morphology and of all sizes.

Figure 8 shows the powders size after they have been sifted to $\leq 53 \mu\text{m}$. Regardless of the powder size, the gas-atomized powders are generally spherical in shape, and the surface is relatively smooth.

Figure 7. SEM image showing the typical powder morphology of the current gas-atomized Pd-10 wt% Rh powders, $\leq 180 \mu\text{m}$.

Figure 8. The SEM image shows the Pd-10 wt% Rh powders after being sifted to $\leq 53 \mu\text{m}$.

Alloy composition

The average Pd and Rh composition of the $\leq 50\text{-}\mu\text{m}$ atomized powders among the 15 lots, measured by WDS, are quite comparable: $90 \pm 3 \text{ at\%}$ and $10 \pm 0.3 \text{ wt\%}$, respectively. The elemental impurity concentration, measured by GDMS, is shown in Table 5. The concentration of all elements, with exception of Pt, is $< 1,000 \text{ ppm}$ and meets the chemical specification shown in Table 2. The Pt concentration in all 15 lots was relatively high, varying from 250 to 1,500 wppm. In many cases, Pt concentration is well above $< 500\text{-ppm}$ limit, which may not be feasible or realistic. The source of Pt is unclear, but it is conceivable that the Pt impurity originates from the raw material obtained from the DOE precious metal pool.

The surface chemical composition was also measured using Auger analysis. The results show small size foreign elements on the powder surface. We were also interested in determining whether or not helium gas had been incorporated into the resultant powders during the He gas atomization. The isotope dilution mass spectroscopy analysis of the UCI mix powders shows the He concentration (Table 6) is quite low, about 0.3 to 0.4 appm.

Table 5. The impurity concentration of the UCI mix powders.

Pd-10%Rh, powder		<i>Shiva ID</i>	
UCI final mix (10)kg		U991	
Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	0.02	Pd	Matrix
Be	< 0.005	Ag	3
B	0.19	Cd	< 0.1
C	~ 20	In	1.1
N	~ 5	Sn	1.3
O	~ 15	Sb	6.2
F	< 0.5	Te	1.1
Na	3.2	I	< 0.05
Mg	1.8	Cs	< 0.01
Al	46	Ba	0.04
Si	13	La	0.02
P	3.7	Ce	< 0.1
S	7	Pr	< 0.1
Cl	0.25	Nd	< 0.01
K	0.55	Sm	< 0.05
Ca	1.2	Eu	< 0.005
Sc	< 0.001	Gd	< 0.005
Ti	0.44	Tb	< 0.005
V	0.16	Dy	< 0.005
Cr	15	Ho	< 0.005
Mn	1.3	Er	< 0.005
Fe	70	Tm	< 0.005
Co	0.32	Yb	< 0.005
Ni	4.6	Lu	< 0.005
Cu	52	Hf	0.13
Zn	1.5	Ta	< 0.5
Ga	0.03	W	0.22
Ge	< 0.05	Re	< 0.01
As	2.8	Os	< 0.005
Se	1.2	Ir	29
Br	< 0.01	Pt	920
Rb	< 0.005	Au	2
Sr	0.02	Hg	< 0.05
Y	0.31	Tl	< 0.01
Zr	7.5	Pb	1.1
Nb	0.02	Bi	0.17
Mo	0.46	Th	0.002
Ru	30	U	0.02
Rh	Matrix		

Surface chemical composition

Figure 9. Auger spectroscopy analysis shows the absence of foreign elements on the as-atomized powder surface.

Table 6. He concentration (atomic ppm).

He concentration by isotope-dilution mass spectroscopy	
UC powder #1	~0.38 appm
UCI powder #2	~0.40 appm

Physical metallurgy

The relevant metallurgical parameters for the as-atomized powders being examined were solidification structure, alloy composition and its uniformity, as well as localized Pd or Rh segregation.

Solidification structure

The optical images of the polished cross sections from the as-atomized powders, $< 10 \mu\text{m}$ to $> 180 \mu\text{m}$, show a characteristic solidification structure as expected. The large size powders, $> 150 \mu\text{m}$, contain dendrites with well-defined primary and secondary dendrite arms while the small size powders, $\leq 50 \mu\text{m}$, contain mostly equiaxed cells (Fig. 10). In general, the secondary dendrite arm or cell boundaries are defined by the last liquid solidified.

In Figure 10, the secondary dendrite arm spacing (SDAS) increased with increasing powder diameter and decreasing cooling rate. The cell sizes of solidification dendrite in the large size powders and the small size powders are $\sim 10\text{--}15\text{ }\mu\text{m}$ and $2\text{--}10\text{ }\mu\text{m}$, respectively (Fig 10).

Figure 10. Optical images of the glycerol etched powders show the well-defined dendrites in the large size powders (left) and equiaxed cells in the small size powders (right).

Chemical uniformity

EPMA / WDS composition profiles across the powder diameters indicate that Rh depletes at the dendrite and/or cell boundaries in all powder sizes, as illustrated in the $>>100\text{-}\mu\text{m}$ powder in Figure 11. This Rh depletion at the dendrite/cell boundaries is consistent with the trend indicated by lever rule from the Pd-Rh binary phase diagram in Figure 1. The solidus and liquidus boundary lines in the phase diagram show the gradual decrease in Rh concentration as the temperature drops.

The WDS analysis for the powders with different size shows a clear trend of Rh depletion; at the dendrite/cell boundaries, Rh decreases with decreasing powder size (Fig. 12). For the $200\text{-}\mu\text{m}$, $75\text{-}\mu\text{m}$, and $40\text{-}\mu\text{m}$ powders, Rh concentration at the dendrite/cell boundary is as low as 7 wt%, 8 wt%, and 9.5 wt%, respectively (Fig. 12). At the same time, Rh concentration can be as high as 12 wt%, 11 wt%, and 10.5 wt%, respectively, at the adjacent matrix of the same boundary. The level of Rh depletion at the boundary was also quantified using the standard deviation of the Rh / Pd weight percent ratio from the WDS measurements (Fig. 13). The plot in Figure 13 shows a continuous drop in the Rh/Pd ratio at the dendrite/cell boundary with powder size.

Figure 11. The SEM image and its corresponding Rh/Pd wt% ratio profile by WDS shows localized variation in alloy composition at dendrite boundaries. The marked line in the SEM image above is the location of the electron beam probe.

Note: the spacing and the locations of the sharp drops in Rh/Pd match the dendrite boundaries spacing and locations.

Figure 12. Typical microstructure in the large and small size powders and Rh composition profile across the dendrite/cell boundary.

Left column: optical image shows the well-defined dendrites in large size powder A ($> 180 \mu\text{m}$), and fine cells in the small size powders B and C ($\leq 50 \mu\text{m}$).

Right column: Rh concentration profile across the diameters of powders A, B, and C show that the Rh depletion increases with increasing powder diameter.

Figure 13. Physical and chemical limits established from the standard deviation of Rh/Pd wt% calculated from the WDS analyses of more than thirty powders of various sizes.

Reproducibility

In order to ensure reproducibility and reliability of the current gas atomization processing, we have performed more than thirty atomization runs. The powders produced from these 30 runs were sifted to $\leq 53 \mu\text{m}$, and the alloy composition and PCT curve were measured and analyzed. The ICP analyses show that the alloy composition among the fifteen randomly picked lots is quite consistent, comparable to the composition of the final UCI mix shown in Table 5. The PCT curves among a randomly picked sample of 10 lots are also consistent and reproducible. The reproducible PCT curve is illustrated in Figure 14, between lot #15 and the UCI mix, through the entire pressure and composition ranges.

Figure 14. PCT curves generated from the product lot #15 and the final UCI mix in 2000 by Meeker were reproducible.

2.4 Hydrogen storage science

2.4.1 Material

The Pd-10 wt% Rh alloy used for the material science study consisted of the powders of $< 50\ \mu\text{m}$ to $\leq 180\ \mu\text{m}$, produced from the current gas atomization system. The typical solidification structure in these powders is shown in Figure 10. Three powders were investigated: as-atomized, 1 H-cycle, and 8 H-cycles. For comparison purposes, we also prepared a reference Pd-10 wt% Rh powder. This reference powder was annealed at $800\ ^\circ\text{C}$ for 2 minutes to remove lattice defect(s) possibly induced from the thermal cooling during the gas atomization.

2.4.2 Hydrogen–metallurgy interaction

Metallurgical evolution and/or changes with respect to surface morphology, microstructure, hardness, and PCT behavior upon H-cycling were examined. Those H-cycled powders are called “1 H-cycle” and “8 H-cycle.” In addition, we prepared heat-treated powders at $800\ ^\circ\text{C}$ for 2 minutes (called “800HT”) for comparing the defect and/or dislocation structures induced by gas atomization.

Effect on surface morphology using SEM imaging

As described earlier, the as-atomized powders are spherical and relatively smooth, with the exception of those areas that intercept the dendrite/cell boundaries (Fig. 15, top row). Upon the H-cycling the powders, the SEM images in Figure 15 show that the overall particle shape remains more or less spherical. However, the surface roughness of the powders has changed with presence of hydrogen. There are deformation slip lines aligned along the crystallographic orientations on the surface of coarse powders ($> 100\ \mu\text{m}$), and a scallop-like surface distortion can be seen on the small size powders ($< 50\ \mu\text{m}$) (Fig. 15, bottom two rows). The surface slip on the small size powders ($< 50\ \mu\text{m}$) was not as obvious as those seen on the large size powders upon H-cycling. The scallop-like morphology appeared to be caused by the volume expansion constraint by those cell boundaries that were exposed to the powder-free surface (Fig. 15, lower right). In summary, the slip lines were observed on a randomly picked H-cycled coarse powder ($80\ \mu\text{m}$) using the SEM imaging at the 10 kx and 50 kx magnification (Fig. 16). The slip lines are more defined on the powders of 8 H-cycles relative to those of 1 H-cycle.

Figure 15. SEM images at 2000x magnification show the effect of the H-cycling on the surface morphology.

Upper row: as-atomized powder shows a relatively smooth surface, except at those locations where the cell boundaries intersected with the free surface.

Middle row: after 1 H-cycle, the large-powder surface contains slip bands and the small size-powder surface contains cell boundary grooves.

Bottom row: after 8 H-cycles, the slip bands on the large size powders and cell boundary grooves on the small size powders become denser and more pronounced.

Figure 16. 5-kV SEM images at magnification of 10,000x (left) and 50,000x (right) illustrate how the surface roughness changes with number of H-cycles.

Note: the slip bands on the large size powders with 8 H-cycles are much more intense and pronounced.

Effect on lattice strain

Lattice strain field using FIB/SEM imaging

SEM imaging of the FIB sliced cross section can be effective for mapping the lattice strain qualitatively. For instance, the FIB/SEM images of the small size as-atomized powder show relatively clean and uniform contrast within each cell (Fig. 17, left column). Upon H-cycling, we observed a complex non-uniform strain contrast within each cell.

The FIB/SEM images at higher magnification in Figure 18 show in greater detail the image contrast between the as-atomized powder and H-cycled powder. Similar to those described in Figure 17, the as-atomized powder displays a relatively clean and uniform image contrast within each cell for powders of all sizes (Fig. 18, upper row). In contrast, the H-cycled powder exhibits localized non-uniform image contrast with feature size $\leq 1 \mu\text{m}$ across the powders. Discovering the source of the strain contrast and explaining the atomistic microstructure evolution requires additional high resolution TEM analysis that are given below.

Figure 17. FIB/SEM imaging is effective for mapping the strain field induced by lattice deformation related to atomic displacement, distortion, and mis-orientation. **Note:** The complex strain contrast is only observed within the cells of the H-cycled powder (right column).

Top row: the as-received powder selected for the FIB/SEM imaging.

Middle row: the FIB cut from the designated locations.

Bottom row: the FIB/SEM images show a uniform contrast of the strain-free cell in the 800 °C annealed powder (left column) and a complex contrast within each cell of the powder subjected to 8 H-cycles (right column).

Figure 18. FIB/SEM images show the 0.5- to 1- μm sized complex lattice strain contrast, induced by H-cycling, within each cell in the powders of all sizes.

Lattice strain using FIB/TEM imaging

The low-magnification TEM/BF images of the 50- μm and 5- μm powders, before and after H-cycling, show a similar lattice strain contrast evolution as shown in the FIB/SEM images in Figure 18. The as-atomized powders are relatively clean and uniform with the exception of a few coarse bend contours. We observed complex loop-like strain contrast throughout the different-size powders subjected to both 1 H-cycle and 8 H-cycles (Fig. 19, arrows). The intensity of the strain contrast loops increases slightly from 1 H-cycle to 8 H-cycles.

Figure 19. FIB/TEM images show the lattice strain evolution induced by H-cycling for the 50- μm and 5- μm powders. The lattice contrast intensity increases as the number of H-cycles increases.

Effect on microstructure using TEM imaging

The TEM/BF images show the as-atomized powder contains a relatively low density of loose dislocations, which were presumably induced during solidification cooling (Fig. 20). In addition, there are fine speckles throughout the sample matrix. These fine speckles are lattice defects

which are believed to be an artifact of FIB damage during the TEM thin-film sample preparation. Upon H cycling (1 H-cycle and 8 H-cycles) the TEM/BF images exhibit a similar high density of dislocations that were tangled and networked throughout the sampling area. In addition, we noticed that the area of dense dislocation networks was highly strained, showing strong strain fields that were often obscured by the dislocation networks (Fig. 20, bottom row arrows). It is also noted that the fine speckles are less visible in the H-cycled matrix, as they are hidden by the strong contrast between the lattice strain field and dislocation tangling. The dislocation entanglement accompanying the strong lattice strain is illustrated in greater detail in Figure 21.

Average spacing between the tangled dislocations (Δd) was estimated from the TEM/BF images of all powders examined, using the line intersect method. The Δd for the as-atomized powder, 1 H-cycle, and 8 H-cycles is ~81, 22 and 24 nm, respectively (Fig. 22). The average dislocation spacing in the H-cycled powders is ~30% of those estimated from the as-atomized powder. Despite the difference in the intensity of the lattice strain seen in the Figure 19, the difference in Δd for the tangled dislocation between the 1 H-cycle and 8 H-cycle powder appeared to be minimal.

Figure 20. TEM/BF images of both 50- μ m and 5- μ m powders show the H-induced dense dislocation networking accompanied by strong lattice strain.

Top row: Typical preexisting loose dislocations in the powder matrix of the as-atomized powders.

Middle row: Dislocation entanglement or networking and lattice strain become evident after 1 H-cycle.

Bottom row: Dislocation networking, accompanied by strong lattice strain, is clearer in the powders subjected to 8 H-cycles.

Figure 21. TEM/BF images at higher magnification show a greater detail of the dislocation networking, accompanied by strong lattice strain, as well as the Δd reduction upon H-cycling.

Figure 22. The enlarged TEM/BF images of the large size powder (50 μm) illustrate the areas selected for estimating the inter-dislocation spacing (Δd).

Effect on the surface morphology using FIB/TEM imaging

FIB/TEM images of the cross section were used to examine the change in surface roughness of the 50- μm powder subjected to H-cycling. The results show that the as-atomized powder is smooth (Fig. 23, upper left) while the H-cycled powders exhibit a progressive increase of extruded steps on the surface (Fig. 23, lower left and lower right). The TEM/BF images also show the extruded steps, located right above the slip lines or dislocation bands underneath. The correspondence of the extruded step with slip band is especially visible in the powder subjected to 8 H-cycles (Fig. 23, middle right). The extruded step spacing is $\sim 10\text{--}15\text{ nm}$, and the step height is minimal for the powder with 1 H-cycle. In contrast, the extruded step spacing and height on the surface of the powder with 8 H-cycles are $\sim 20\text{--}30\text{ nm}$ and $\sim 10\text{--}15\text{ nm}$, respectively. These extrusion step dimensions are comparable to those slip lines seen on the powder surface revealed by SEM image shown in Figure 23 (upper right inserts). It should be

noted that the extrude steps seen here is resemble to those fatigue striations often seen in the metal systems. (Ref.6).

Figure 23. TEM/BF images show the surface roughness increasing with increasing number of H-cycles (left column). The enlarged images in the right column demonstrate the correspondence between the extruded steps and the slip line underneath for the 50- μm powders subjected to 8 H-cycles. The upper inserts are SEM images of the 50- μm powder surface with 1 and 8 H-cycles.

2.4.3 Vicker's microhardness

Vicker's microhardness is calculated based on Vicker's diamond indent size. For a statistical representation, the average Vicker's microhardness was calculated from the measurements of five relatively large ($\sim 50\ \mu\text{m}$) powders. The diamond indentation was performed using both 10-gram and 25-gram loads. The results presented in this report are the average Vicker's hardness number (VHN) of the five measurements.

The results show a progressively increasing hardness from 800 °C annealing, as-atomized, 1 H-cycle to 8 H-cycles (Table 7). This trend is also illustrated qualitatively by the decreasing diamond indent size (Fig. 24) and quantified in Table 7 and the plotted chart in Figure 25. The most significant hardness increase was between the as-atomized and 1 H-cycle powders. In general, the hardness at the 25-gram load increases by a factor of 2–3 times after being subjected to H-cycling. In addition, the SEM images show the brittle shear band around the edge of diamond indents of the H-cycled specimens.

The hardnesses measured using the 10-gram load are slightly lower than those measured using 25-gram load. The lower Vicker's hardness readings using the lighter 10-gram load are measurement artifacts attributed to underestimation of the small size, poorly defined diamond indents.

Figure 24. The SEM images illustrate decreasing Vicker's indent size for the powders from the 800 °C annealed, as-atomized, 1 H-cycle, and 8 H-cycle powders.

Note: the brittle shear bands seen around the diamond indents occur only in the H-cycled powders (see the arrows in the lower images).

Table 7. Vicker's microhardness by Vicker's diamond indentation.

Indent load	HT 800C	As Recd	1 H-cycle	8 H-cycles
25-grams	75.60	97.5	172.6	194.7
10-grams	42.9	107.2	152.5	171.6

Figure 25. The plot illustrates that the Vicker's microhardness increases with increasing number of H-cycling for both 10- and 25-gram loads.

2.4.4 Lattice strain and deformation by XRD

The relative lattice strain discussed in this report is compared against the XRD peaks for the powders that were annealed at 800 °C for 2 minutes. Compared to the XRD spectra with the spectrum from the 800 °C annealed powders, the widths of all the XRD peaks are broadened, especially those at high 2θ angles (Fig. 26). The full width half maximum (FWHM) of each peak was calculated based on the spectra in Figure 26 as shown in Table 8. There is a clear trend of progressive increases in peak broadening with the number of H-cycles for all peaks including (111), (200), (220), and (222). The increase in FWHM varied by a factor of 2 to 4 depending on the 2θ angle of the peak. In general the changes are less revealing at a low 2θ angle peak. The increase in peak broadening is much steeper between the as-atomized and 1-H-cycle powders. These changes in peak broadening are indicative of H-induced lattice displacement and/or imperfection due to plastic deformation. This trend is consistent with those described earlier for the hardness measurements.

Figure 26. Progressive XRD peak broadening observed from the powder sample with 800 °C/2minutes annealing (top), as atomized (2nd), 1-H cycle (3rd), and 8-H cycle (bottom).

Table 8. Peak broadening calculated from the XRD spectra in Figure 26.

		XRD 111	XRD 200	XRD 220	XRD 222
Sample ID	Cyles	FWHM (deg)	FWHM (deg)	FWHM (deg)	FWHM (deg)
800°C Annealed	-1	0.19	0.23	0.25	0.16
As received	0	0.21	0.27	0.34	0.4
1 H-Cycle	1	0.28	0.53	0.58	0.68
8 H-Cycles	8	0.3	0.58	0.63	0.71

Figure 27. XRD peak broadening increases with the number of H-cycles.

Note: Cycle -1 corresponds to the sample of 800 °C annealing, and cycle 0 corresponds to the sample of as-atomized powder.

2.4.5 Hydrogen absorption-desorption behavior

It should be mentioned that the isotherm PCT behavior of the UCI mix powders was examined three times between FY2000 to FY2010 by different groups in SNL/CA, using different instruments. The PCT curves of UCI mix Pd-10 wt% Rh powders generated from the above three systems are quite consistent and reproducible, as illustrated in Figure 28. The hydrogen absorption-desorption PCT curves are not fully reversible and they also exhibit a hysteresis loop. The starting absorption and desorption plateau pressures measured in 2000 and 20001 were ~0.3 atm and ~0.2 atm respectively (Fig. 28, upper). The starting plateau pressure measured in 2010 (recorded in mmHg) agrees with the two earlier PCT curves described above. The starting absorption and desorption plateau pressures are ~250 mmHg (~0.3 atm) and ~150 mmHg (~0.2 atm) respectively (Fig. 28, lower). In all cases, the plateau pressure for both absorption and desorption are relatively smooth and slightly inclined.

A PCT curve was also obtained recently for the UCI mix powders subjected to 8 H-cycles, using the commercial system. The shape of the hysteresis loop for the powders of 8 H-cycles is very similar to those for 1 H-cycle (Fig. 29). It is worth mentioning that the size of the hysteresis loop for the 8 H-cycles appeared to be slightly narrower. The plateau pressure is slightly lower for absorption and higher for desorption, with a difference of ~30 mmHg. The hysteresis effect that is observed here is due to plastic deformation of the system that dissipates energy, and the amount of this energy is represented by the area of the hysteresis loop in the figure. The repeated cycling of the hydrogen loading and unloading is mechanically equivalent to repeated cycling during fatigue. This is consistent with the observations of increased dislocation density and the steps that form on the surface of the powders (Ref 6).

Figure 28. PCT curves generated from the three different groups in SNL/CA. Upper left by D. Meeker in 2000 using the custom designed manual operation; upper right by K. Gross in 2001 using a customer-designed fully computer-automated operation; lower by M. Ong in 2010 using the existing commercially available system.

Note: the shaded areas show the reproducible PCT curve by Meek and Gross using different instruments, under the same pressure and concentration range.

Figure 29. The PCT curve for the powders subjected to 8 H-cycles.

Note: the PCT curve for the powders subjected to 1 H-cycle is superimposed on the same chart for comparison purposes. The hysteresis loop for the 8 H-cycle powder is slightly narrower.

3 Summary and discussion

3.1 Material synthesis and process optimization

- In collaboration with Professor E. Lavernia, we have developed a supersonic atomization system. This system has produced Pd-10 wt% Rh powders that meet the low chemical segregation and impurity requirements (Fig. 30 a-b) (Ref. 2-5).
- The extensive experimental test runs and data analysis enabled us to establish gas atomization processing–metallurgy–PCT relationship. Such a relationship was essential for optimizing the system hardware configuration and processing parameters that led to the following technical achievements:
 - The customer designed the 18-hole supersonic helium gas atomizer and multi-layer composite nozzle to achieve cooling rate to 10^6 °C/sec.
 - This fast cooling allows us to minimize Pd segregation to ≤ 1.0 wt% for the Pd-10 wt% Rh powders, ≤ 50 μm (Fig. 30 c). According to Guthrie (Ref 7), this uniform alloy composition is crucial to maintaining an adequate and consistent hydrogen plateau pressure for the Pd-Rh H-storage system.
 - The current scientific exercise led to the establishment of the final specifications for powder size, ≤ 50 μm , elemental segregation limit, ≤ 1.0 wt% Rh depletion, and impurity concentration (Table 3). These specifications are achievable and reproducible for Pd-10 wt% Rh for H-storage (Fig. 30 d-e).
 - We have successfully atomized 14 kilograms of Pd-10 wt% Rh powders for the R&D activities and the Pd-Rh material synthesis capability is now established in late 2000.
 - One shortcoming of the current atomizer is the relatively low achievable production yield (~ 45 – 50%) of the ≤ 50 - μm powders that need to be improved.

Figure 30. The overall design, construction, and system performance of the helium gas atomization system constructed at UC Davis, through the SNL/CA–UC Davis collaboration. (a) System configuration; (b) SEM image of the powder the system produced; (c) relatively low chemical segregation (± 1 wt %); (d) reproducible PCT curve generated between the Lot 15 and UCI final mix; (e) The powder size and Rh concentration variation limit specified based on the current scientific analyses.

3.2 Material science of H-storage

The correlation between metallurgical properties and isotherm hydrogen absorption and desorption PCT behavior of the UCI mix powders was examined extensively. Upon the H-cycling, we observed the following:

- Upon H-cycling, the absorption-desorption PCT curve is not always fully reversible (Fig. 31). The PCT curve exhibits a hysteresis loop with a slightly inclined plateau pressure, which is indicative of minor Pd segregation during solidification. There is minimal change in the PCT curve with respect to plateau pressure, H-capacity, and hysteresis loop size between 1 H-cycle and 8 H-cycles.
- Slip bands on the surface of the large size powders and scallop-like cell distortions on the small size powders were observed and attributed to the plastic deformation and/or volume expansion induced by the hydrogen cycling (Fig. 32 a-b).
- Strong localized strain fields were seen in the powder matrix. Analysis of the XRD, Vicker's hardness, and TEM/image analyses illustrated in Figure 33 suggests that the strain field resulted from the combination of H-induced lattice volume expansion, distortion/displacement, and dislocation networking.
- The current results also show the PCT and H-induced metallurgical evolution took place mostly during the first H-cycle and remains relatively stable beyond the first H-cycle.
- Compared to the $\leq 50\ \mu\text{m}$ gas-atomized powders, the PCT curve from the chemically precipitated nano Pd-10 wt% Rh powders ($\leq 30\ \text{nm}$) possesses an extremely narrow hysteresis loop and high plateau pressure slope (Fig. 34 a-f). In addition, the nano powders contain 1- to 5-nm internal pores (Ref. 8). It is suspected that the narrow hysteresis loop may be attributed to the inability of the nanopowders to accommodate the H-induced dislocations and their networking, and the latter is attributed to the non-uniform alloy composition.

Figure 31. Comparison of PCT curves between 1 H-cycle and 8 H-cycles shows minimal changes in hysteresis loop shape and size.

Figure 32. SEM images show H-induced powder surface roughening.
(a) The large-powder surface contains slip bands and (b) the small size-powder surface contains scallop-like distortions.

Figure 33. The experimental data composite illustrates the H-induced metallurgical evolution and its implication to PCT behavior, hysteresis loop in particular.

Center: Typical PCT curve of the as-atomized powders.

Upper left: TEM imaging of strain field.

Upper right: XRD line broadening indicating lattice displacement, expansion, and/or distortion.

Lower left: Dislocation networking.

Lower right: Vicker's hardness and peak broadening increases with H-cycling.

Figure 34. Comparison of metallurgy and PCT behavior between the 50-μm gas-atomized powders with chemically precipitated 30-nm nanopowders. The PCT result and TEM/BF images of the nanopowders were generated by M. Ong, D. Robinson, and B. Jacobs (Ref. 8).

a-b: SEM images show the differences in powder morphology.

c-d: PCT curve shows the difference in the hysteresis loop and plateau pressure slope.

e-f: TEM/BF images show the H-induced dislocation networks in the gas-atomized powders and the nanoporous structure of the as-received precipitates.

In short, there is a strong correlation between the metallurgy and PCT behavior of the Pd-10 wt% Rh powders. We believe that the dislocation introduced by H-induced plastic deformation is responsible for the PCT behavior observed in this study. We expect that these findings will lead to two journal publications, one article describing the correlation of the hysteresis with plastic energy dissipation and fatigue of the material, and another article which describes the effects of cryomilling on the structure and PCT properties of the alloy.

4 Conclusions

- A supersonic fast-cooling gas atomization system was developed for production of Pd-10 wt% Rh powder for the R&D activities at SNL, CA. This atomizer can produce powders with minimum Pd segregation that allow the H-storage system to maintain an adequate and consistent hydrogen plateau pressure during operation. This gas atomization technology has been transferred to the production facility at SRNL.
- Dislocations and their networks are introduced by H-induced plastic deformation during H-cycling. This plastic deformation is responsible for the large hysteresis loop of the isotherm absorption and desorption PCT curve of the Pd-10 wt% Rh powders. This conclusion is consistent with the hypothesis of plastic deformation controls hysteresis loop suggested by others.
- The extensive powder atomization test runs and H-storage study enabled us to determine the final specification for powder size, Pd segregation limit, and impurity level of Pd-10 wt% alloy.

5 Future work

In order to gain a better understanding of He-Pd-Rh alloy interactions, we are engaging in the following scientific activities:

- Conducting a feasibility study of making nano-scale powders through cryomilling of the existing Pd-10 wt% Rh atomized powders.
- Examining the H-storage behavior of cryomilled nanopowders and its comparison to the nanopowders through chemical precipitation processes.

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