Hydrogen sorption characteristics of nanostructured Pd-10Rh processed by cryomilling

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Abstract

Palladium and its alloys are model systems for studying solid-state storage of hydrogen. Mechanical milling is commonly used to process complex powder systems for solid-state hydrogen storage; however, milling can also be used to evolve nanostructured powder to modify hydrogen sorption characteristics. In the present study, cryomilling (mechanical attrition milling in a cryogenic liquid) is used to produce nanostructured palladium-rhodium alloy powder. Characterization of the cryomilled Pd-10Rh using electron microscopy, X-ray diffraction, and surface area analysis reveals that (i) particle morphology evolves from spherical to flattened disk-like particles; while the (ii) crystallite size decreases from several microns to less than 100 nm and (iii) dislocation density increases with increased cryomilling time. Hydrogen absorption and desorption isotherms as well as the time scales for absorption were measured for cryomilled Pd-10Rh, and correlated with observed microstructural changes induced by the cryomilling process. In short, as the microstructure of the Pd-10Rh alloy is refined by cryomilling: (i) the maximum hydrogen concentration in the α -phase increases, (ii) the pressure plateau becomes flatter, and (iii) the equilibrium hydrogen capacity increases at pressure of

101.3 kPa . Additionally, the rate of hydrogen absorption was reduced by an order of magnitude compared to non-cryomilled (atomized) powder.

1 Introduction

Hydrogen is a flexible method of storing and transporting energy; when combined with renewable energy sources, hydrogen technology represents an attractive alternative to traditional fossil fuels [1]. Solid-state storage of hydrogen has many advantages compared to gaseous and liquid storage, including increased volumetric efficiency [2]. One of the most promising hydrogen storage methods is through reversible metal hydrides. Palladium and its alloys are convenient model systems for understanding hydrogen storage behavior in metal-hydrides as they can store significant amounts of hydrogen near ambient conditions.

In metals, a reduction of size of grains and subgrains (or crystallites) can lead to changes in physical and mechanical behavior. In particular, metals with nanometer-sized grains feature higher strength than conventional metals [3,4] as well as significant changes in physical behavior, including changes associated with the formation of hydride phases when exposed to hydrogen [5]. In the past several decades, numerous methods have been developed to synthesize polycrystalline metals with small grain sizes including inert gas condensation [3,6,7] and severe plastic deformation (SPD) [8–10]. Polycrystalline materials are typically classified by their average grain size: while coarse-grained (CG) materials typically have grain sizes on the order of tens of micrometers, ultrafine grained (UFG) materials are defined as materials with grain sizes in the range of 100-500 nm, and nanostructured (NS) materials feature grain sizes with at least one dimension that is less than 100 nm.

Decreasing the grain size in metal-hydrogen systems provides insight to the mechanisms of absorption and reaction of hydrogen in metal hydride formers. Observed changes in hydrogen sorption properties have been attributed to the increased grain boundary volume in NS-material compared to CG-material [11–13]. Palladium and magnesium, in particular, are common model

metal hydride systems. Krystian *et al.* [14] and Skripnyuk *et al.* [15] produced bulk UFG-Mg alloys with an average grain size of 250 nm by equal channel angular pressing (ECAP); their materials exhibited faster absorption and desorption, though this came at the expense of a reduction of the equilibrium hydrogen content. Despite the observed acceleration of the kinetics of absorption and desorption, hydriding and de-hydriding of UFG-Mg and Mg alloys remain too slow for practical applications [16]. In NS-Pd (average grain size of 5 nm produced using inert gas condensation), the equilibrium hydrogen content at dilute H/M concentrations was improved compared to CG-Pd [11,17]; however, the hydrogen content at higher pressure was reduced [6,12,17].

Recently, Bérubé and coworkers [5,16] proposed that NS powder has significantly different energetics and kinetics of hydride formation because of greater total surface energy of NS powder, which includes increases of both the grain boundary volume and specific surface area (from a decreased particle size). Their study demonstrated that the size and geometry of particles can affect the enthalpy of hydride formation, and that the surface area-to-volume ratio is critical for determining the enthalpy of formation, especially when particle sizes can be reduced to tens of nanometers or less.

Mechanical milling (also known as ball milling) is an attractive method of processing metallic powders for hydrogen storage because of the ease of implementation and scalability [18,19]. The deformation imparted to a material during mechanical milling results in microstructural refinement through plastic deformation. Previous studies have explored mechanical milling to process NS-Mg and Mg-based compounds/alloys for hydrogen storage [13,20–22]. Zaluska *et al.* [20] found that mechanical milling was an effective process to improve the morphology of the powders and surface activity for hydrogenation, as well as for

dispersing and embedding catalytic agents such as Pd nanoparticles into the surface of the milled Mg particles. It is important to recognize that milling processes can, at best, reduce crystallite sizes to tens of nanometers, while the size of particles generally remains large (on the order of microns due to agglomeration and cold welding of particles during the milling process) [18,19,23].

In the present study, UFG-Pd alloy was produced using a variation of mechanical milling, known as cryomilling. Cryomilling is mechanical attrition ball milling in a cryogenic slurry [24] containing a cryogenic liquid, the milling media, and the powder being milled. This technique has been shown to be effective for achieving modified morphologies and microstructures in many material systems including aluminum and its alloys [24–26], nickel superalloys [27], and zinc-aluminum alloys [23]. Faster rate of microstructural refinement is a primary advantage of mechanical milling at cryogenic temperatures. The cryogenic temperature reduces the rate of recovery and recrystallization that would otherwise result from heat generated during the milling process [28]. Thus, in comparison to milling at room temperature, cryomilling achieves smaller average grain sizes in shorter periods of time.

The present study was undertaken to provide insight into the mechanisms of hydrogen sorption in metal-hydride systems. In particular, a binary Pd-10Rh alloy was cryomilled, and the physical properties, such as particle morphology, microstructure and lattice defects, are characterized. The equilibrium hydrogen pressure-composition isotherms of the cryomilled powder are also described and related to the microstructural properties induced by cryomilling. These observations are then used to provide insight to the mechanisms of hydrogenation.

2 Experimental Procedures

Pd-10Rh (wt%) was selected for study because it features greater hydrogen storage capacity and plateau pressure than pure Pd [29–31]. The starting Pd-10Rh powder was synthesized using high velocity spray atomization, as reported previously [31–33]. The atomized powder was cryomilled in a Union Process 1-S attritor (Union Process, Akron OH) using a stainless steel milling vessel and stainless steel milling balls as the milling media. Liquid Ar was used as the cryogen, and cryomilling was conducted for 1, 2 and 8 hours with a ball-to-powder mass ratio of 32:1. Additionally, approximately 0.2 wt% of stearic acid was used as a process control agent (PCA) in order to mitigate cold welding between the alloy particles during cryomilling.

The atomized and cryomilled Pd-10Rh powders were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). For the microstructural characterization, powder samples were prepared using conventional metallographic techniques. After mounting and polishing, cross-sections of the atomized and cryomilled Pd-10Rh powders were analyzed using a JEOL 7600 microscope (JEOL Ltd., Tokyo, Japan) operating at 15 kV. The XRD patterns were recorded on a PANalytical Empyrean X-ray diffractometer equipped with a PIXcel^{3D} detector and operated using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scattering intensities were measured using the Bragg–Brentano (θ - 2θ) geometry over an angular range of $30^\circ < 2\theta < 120^\circ$ with a step size of 0.026° . Thin film samples for TEM were prepared using focused ion beam (FIB) in a FEI Dual Platform Helios NanoLab. TEM analysis was performed using a FEI CM30 at 300kV.

Surface area measurements (Brunauer, Emmett and Teller (BET) method) and pressure-composition (PC) isotherms were determined using a Micromeritics ASAP 2020 porosimeter.

Samples were degassed for 15 hours at 50°C prior to surface area measurements using krypton gas at 77 K as the adsorbent. Krypton was used as the adsorbent gas to improve the resolution of the BET measurement because of the low surface area of the particles. Approximately 150 mg of powder was used in each of the hydrogen absorption experiments. Prior to hydrogen absorption experiments, sample surfaces were cleaned by three cycles of exposure to gaseous hydrogen gas at room temperature, each cycle consisting of hydrogen partial pressure of 1.1 kPa followed by evacuation. This surface cleaning procedure was used primarily to remove surface oxides (cleaning may also mitigate the potential surface effects of the liquid Ar exposure during cryomilling). For PC isotherm measurements, equilibrium was defined as changes in hydrogen pressure <0.01% over 30 second intervals. Rates of hydrogen uptake were measured by loading the porosimeter manifold with gaseous hydrogen to pressure of ~120 kPa, opening the valve to the sample holder and recording the pressure drop at 25°C. After correction for near instantaneous expansion into the larger volume, pressure drop was converted to moles of hydrogen atoms and attributed to absorption by the Pd-10Rh alloy powder. The equilibrium (final) pressure after these uptake experiments varied between 68 and 71 kPa among the samples.

3 Results and Discussion

3.1 Particle morphology

The atomized particles are spheroids in shape with a nominal diameter of around 20 μm , as shown in SEM images of the powder (Figure 1a) and in cross section (Figure 1e). During cryomilling, the Pd-10Rh particle morphology evolved from the spherical atomized particles (with an aspect ratio near one) to high aspect-ratio, disk-shaped flakes with a diameter near 100 μm (Figures 1b-d, 1f-h). The specific surface area evolved during cryomilling, increasing from 0.037 m^2/g for the spherical atomized particles to 0.44 m^2/g after 8 hours of cryomilling

(Table 1). For comparison, the theoretical surface areas of a smooth sphere of 20-micron diameter and a disk of equal volume with a diameter of 100-micron are $0.025 \text{ m}^2/\text{g}$ and $0.32 \text{ m}^2/\text{g}$, respectively. As cryomilling proceeds the surface area increases approximately linearly with time.

Particles are flattened when milling balls impact particles between other balls or the wall of the vessel. In addition to normal strains from collisions between particles and the milling media, cryomilling introduces shear deformation as a result of the attrition milling configuration [18,19,34]. In attritor milling, the powder and milling media (i.e., stainless steel balls) are rotated within the vessel, imparting shear strains during ball-particle impacts [34,35]. Through a combination of normal and shear forces, the particles become elongated and flattened. In studies of other cryomilled materials, fracture and cold welding occur concurrently leading to approximately equiaxed particles [23,24,27]. While commonly observed for other metals cryomilled for similar durations of time [18,19,23,27], particle fracture did not evolve in the same way in the present study. While the longer cryomilling times show greater amounts of smaller particulate and debris (Figure 1h), which presumably is related to fracture of the flakes, overall the cryomilled particles maintain flattened disk shapes without evidence of the typically observed fracture/welding process. This unique characteristic of Pd is attributed to its ductile nature [7].

3.2 Microstructural evolution

TEM observation of the atomized and cryomilled Pd-10Rh powder provides insight into the mechanisms responsible for the observed changes in microstructure caused by cryomilling. The microstructure of the atomized particles appears homogenous with a small population of dislocations that formed during atomization and rapid solidification (Figure 3a) and with

relatively few boundaries. Cryomilling generates dislocation tangles and sub-boundaries, as well as strain field contrast, all of which gradually intensify with increased milling time. These features are apparent in the micrographs shown in Figures 3b and 3c for powder cryomilled for 1 and 2 hours, respectively. A large number of boundaries evolve during cryomilling, including elongated subgrains observed along the length of the particles. It was not possible to estimate the average length of the sub-grains by TEM due to a limited population of boundaries within a single particle. The width of the sub-grains after 1 and 2 hours of cryomilling, however, was estimated to be approximately 400 nm and 300 nm, respectively. Cryomilling for 8 hours led to further sub-grain refinement to approximately 100 nm (Figure 3d), while the length of the sub-grains was estimated to be around 1 μm . A high density of dislocations was observed in the interior of the grains after cryomilling. These observations are consistent with the XRD measurements described below.

Witkin and Lavernia [24] described microstructural refinement in materials processed using ball milling techniques (including cryomilling) as similar to that of materials processed using other types of bulk SPD techniques, such as ECAP, high pressure torsion, and cold rolling. The microstructural refinement observed in the cryomilled Pd-10Rh particles is similar to the plasticity-induced grain refinement that is observed in other face-centered cubic metals, such as Cu [36–38]. During severe plastic deformation, dislocations nucleate in the material and move under the influence of the applied shear stresses. These dislocations can entangle to form dislocation substructures, annihilate [37], or migrate to boundaries and contribute to misorientation of these boundaries [38]. The continued evolution and interaction of dislocations with further deformation subdivides grains and sub-grains resulting in the microstructural refinement process [37]. The characteristic dimensions of microstructure are reduced with

continued cryomilling until the grain size saturates at a minimum value, which is dependent on several material parameters including stacking fault energy, equilibrium distance between two edge dislocations, milling temperature, and composition [39–41]. Evidence of microstructural saturation (such as equiaxed grains and a high concentration of high angle grain boundaries) was not found for cryomilling times up to 8 hours in Pd-10Rh, suggesting that smaller sub-grain sizes can be achieved.

Phase identification and dislocation density were determined using XRD pattern analysis. The XRD pattern of the atomized powders confirms a solid solution in the starting Pd-10Rh alloy; moreover, the solid solution is maintained during cryomilling (Figure 2). Compositional segregation on the secondary dendritic arms in the atomized Pd-10Rh has been previously reported [31,32], although segregation was not observed in this study. Segregation, if it exists, is below the detection limit of XRD. XRD peak broadening is observed with a trend of progressive broadening as cryomilling time is increased. This peak broadening can be attributed to microstructural refinement (a decrease in the size of subgrain structures, also called crystallites) and lattice strain induced by dislocations as reported by Ungár [42] and Zhao *et al.* [43,44]. In order to deconvolute both crystallite size and strain-related broadening effects, the XRD patterns were analyzed using a simplified integral breadth method. The full width half maximum of each peak was measured using the Pearson VII function, and fitted according to a modified Williamson-Hall relationship [43,45]. The dislocation density ρ was then calculated from the following equation [44]:

$$r = \frac{2\sqrt{3}\langle\epsilon^2\rangle^{1/2}}{Db} \quad \text{Eq. [1]}$$

where lattice strain (ε) and crystallite size (D) were previously determined from the Williamson-Hall analysis [46], and b is the magnitude of the Burgers vector in the Pd-10Rh alloy (0.274 nm). The results of the XRD line profile analysis on the Pd-10Rh powder are summarized in Table 1, which shows clear trends of reduction in crystallite size, increased microlattice strain, and greater dislocation density with increasing cryomilling time. In particular, cryomilling leads to gradual refinement of the subgrain structure with increased milling time: from 230 nm for the atomized powder to 77 nm after 8 hours of cryomilling.

Even though dislocations tend to migrate to grain boundaries or dislocation substructures, there is still a high concentration of residual dislocations located within the interior of the subgrains [36]. Zhao et al. found that in mechanically milled Fe and Cu, the dislocation densities measured using XRD profile analysis increased from $\sim 10^{14} \text{ m}^{-2}$ to $\sim 10^{15} \text{ m}^{-2}$ after similar milling times [43,44]. In the present study, the dislocation density measured by XRD increased with longer cryomilling time, from $1.2 \times 10^{14} \text{ m}^{-2}$ in the atomized powder to $2.4 \times 10^{15} \text{ m}^{-2}$ after 8 hours of cryomilling; the presence of a high concentration of dislocations is also apparent in TEM micrographs (Figure 3). In addition to the strain contrast created by dispersed dislocations, dense dislocation walls are observed in the TEM micrographs in Figures 3b and 3c.

3.3 Equilibrium hydrogen sorption characteristics

PC isotherms, shown in Figure 4, are used to compare the hydrogen storage characteristics of the different Pd-10Rh powders. At very low pressure, hydrogen is soluble in the defect structure of the Pd-10Rh alloy (especially at free surfaces) and characterized by the hydrogen concentration extrapolated to zero pressure; this value is referred to as θ_{max} . The conventionally-defined α -hydride phase, which exists at low concentration of hydrogen, is characterized by a maximum concentration of hydrogen denoted α_{max} and defined as the

intersection of extrapolations of the low-pressure portion of the PC isotherm and the plateau portion of the PC isotherm. The plateau pressure, which represents the transformation of the α -hydride to the β -hydride ($\alpha \rightarrow \beta$), has a slightly positive slope for these materials, thus the transformation in these materials occurs over a range of pressure (albeit a small range). The minimum hydrogen concentration of single-phase β -hydride ($\beta_{\min}$) is difficult to establish from the PC isotherms, but appears to differ for the different powders. For the purposes of comparing the powders at high hydrogen concentration, the equilibrium hydrogen concentrations (c_H) at pressure of 80 kPa and 101 kPa are used to demonstrate the differences between the different powders. The concentrations of these transitions ($\theta_{\max}$, $\alpha_{\max}$, and c_H) are summarized in Table 2 for each powder.

The hysteresis in the PC isotherms is attributed to dislocation generation during hydrogen absorption/desorption as described in Ref. [47]. The observation that the size of the hysteresis loop is not a function of the cryomilling is consistent with unsaturated dislocation structures (and the continuous evolution of dislocation density with cryomilling time, Table 1). In contrast, if dislocation structures are saturated, as described Eckert et al. [40] and Pippan et al. [41], resistance to formation of additional dislocation structures may impede phase transformations, thus affecting hysteresis. In the present investigation, the refined microstructures of the cryomilled Pd-10Rh do not appear to be saturated, based on the principles set forth by Mohamed [39], thus significant effects on the phase transformation and hysteresis seem unlikely. Recently, Cappillino et al. investigated the effect of multiple hydrogen-loading cycles on atomized Pd-10Rh, and found that subsequent cycles caused only modest changes to the shape of the PC isotherms [47]. The unsaturated dislocation structures of the cryomilled Pd-10Rh in the current study suggests that slight changes to successive PC isotherms (such as increases in α -phase

solubility) could be expected consistent with the findings of Cappillino et al., while large differences in the hysteresis will require more aggressive cryomilling to saturate dislocation density in the material. This topic is the subject of an ongoing study, and the effect of hydrogen-loading cycles on PC isotherms of cryomilled Pd-10Rh will be presented in a forthcoming study.

A sloping plateau pressure has been previously attributed to several factors in alloys and intermetallics, including compositional inhomogeneity in the sample [48,49]. In the cryomilled samples, the slope of the plateau is reduced with longer cryomilling time, which suggests a reduction of the inherent segregation in the Pd-Rh solid solution. Longer cryomilling time refines the microstructure, effectively decreasing the secondary dendrite arm spacing relative to the original solidified microstructure. While the atomized powder for this study was selected to have minimal segregation [31,32], some segregation in the atomized powder likely exists, although compositional segregation was not detected in the atomized or cryomilled powders. A plateau that varies between about 40 and 80 kPa is observed here, which agrees well with previous studies on hydrogen absorption in Pd-10Rh alloys [29]. In addition to the sloping pressure plateau, a large increase in the pressure of the plateau region is observed for the Pd-10Rh alloy compared to pure Pd. Previous work has attributed the increased plateau pressure to lattice contraction upon alloying and the additional strain energy that must be overcome as hydrogen occupies octahedral sites [29]. This interpretation can be extended to understand the decrease in pressure of the plateau for longer cryomilling times, while maintaining the overall features of the PC isotherms. The internal strain (Table 1) that is introduced during the cryomilling process is essentially a dilation of the lattice, opposing the effect of alloying. In other words, greater lattice strain due to longer cryomilling times flattens the pressure plateau by offsetting lattice contraction associated with alloying.

At very low pressure, differences in hydrogen uptake are apparent for the atomized and cryomilled samples as characterized by $\theta_{\max}$. Because the large, negative heat of chemisorption is greater than the heat of absorption, the lag at very low pressure (dilute concentrations) must correspond to occupation of surface and sub-surface sites as well as other traps such as vacancies, grain boundaries and dislocations [50]. The surfaces, in particular, can act as low pressure traps for hydrogen, adsorbing hydrogen to the surface of the particle before being absorbed into the material [51]. The parameters $\theta_{\max}$ and $\alpha_{\max}$ are plotted in Figure 5 as a function of BET surface area, showing an approximately linear trend between surface area and hydrogen concentration for both parameters. In addition to increasing internal strain, longer cryomilling time increases the surface area of the particles (Table 1), thus these trends also correlate with cryomilling time. While it seems reasonable to attribute the increase in $\theta_{\max}$ to greater surface area, the correlation between surface area and $\alpha_{\max}$ makes less physical sense. In the case of $\alpha_{\max}$, the bulk alloy (rather than surface) must interact with hydrogen, as implied by the magnitude of the hydrogen concentration. Additionally, although perhaps a portion of the increase of $\alpha_{\max}$ is related to surface area, the greater slope of the concentration-surface area curve in the case of $\alpha_{\max}$ compared to $\theta_{\max}$ (Figure 5) suggests another explanation.

Previous studies have shown that the presence of dislocations can increase the equilibrium hydrogen content in the α -hydride phase [52,53]. In the present work, cryomilling substantially increases the dislocation density and this increase is approximately linear with cryomilling time (Table 1). The parameters $\alpha_{\max}$ and C_H (at 101 kPa) are plotted in Figure 6a as a function of dislocation density. A basic trend of increasing hydrogen concentration for both parameters with greater dislocation density is apparent in general agreement with several reports in the literature [53–55]. However, other studies have attributed increased equilibrium hydrogen

content to grain boundary volume [6,11,17]. Assuming that subgrain boundary volume scales with $1/D$, similar correlations can be established between hydrogen content and subgrain boundary volume, as shown in Figure 6b. In addition, since $\theta_{\max}$ was attributed to surface area effects, we correct the hydrogen content in the hydride phases by subtracting the contribution from $\theta_{\max}$ in this figure ($\alpha_{\max}$ is also plotted for comparison). Both dislocation density and grain boundary volume correlate well with hydrogen content in the α -hydride phase; therefore, the respective contributions of dislocations and boundaries cannot be established based on these results.

Hydride formation can induce dislocation densities comparable to those created by heavy cold work in metallic systems [30,56,57], thus the starting dislocation density may not reflect the *in situ* dislocation density during hydrogen exposure at the higher pressures considered in this study. Nevertheless, C_H (at 101 kPa) appears to correlate better with the initial dislocation density than subgrain boundary volume (compare Figures 6a and 6b), suggesting perhaps that equilibrium hydrogen content (at least at a fixed pressure) is not strongly dependent on the subgrain boundary volume. Indeed, when the crystallite size is reduced from several microns to 100 nm, the subgrain boundary volume in the material is increased from a negligibly small volume to approximately 3% of the material [58]; further reduction of crystallite size will substantially increase the volume of subgrain boundaries and, thus, the influence of these boundaries. In this study, C_H (at 101 kPa) appears to be reaching saturation at the smaller crystallite size, rather than being augmented at the smaller crystallite size, implying that boundary volume is not a dominant factor for hydrogen capacity. Quite the opposite is observed for metals with smaller average crystallite size (less than 50 nm), where the equilibrium

hydrogen content at high pressure (β -hydride) is reported to be greatly diminished even though higher $\alpha_{\max}$ was observed [6,11,17].

3.4 Rate of hydrogen uptake

The rates of hydrogen uptake for the different cryomilling times were calculated by normalizing the instantaneous H/M molar ratio with the equilibrium H/M molar ratio, and plotting as a function of time (Figure 7). The half-life of the hydrogen uptake process is compared in Table 2 for each cryomilling condition. The cryomilled powders absorb hydrogen faster than the atomized powder, by a factor of 3 and 2 for the powders that were cryomilled for 1 hour and 2 hours, respectively. Absorption was 10 times faster for the powder that was cryomilled for 8 hours. The rate-limiting step in the hydrogen absorption process in palladium is still debated [59]. Three elementary steps are generally considered in the mechanism of absorption of hydrogen gas into a metal lattice: (i) dissociative chemisorption, (ii) absorption from the surface into subsurface sites, and (iii) bulk diffusion [60]. The increased rates of hydrogen absorption with greater cryomilling time observed in the present study can be explained by the increase in surface area-to-volume ratio if either chemisorption or transfer to subsurface sites is rate-limiting. If diffusion is rate limiting, then rates of hydrogen uptake will be controlled, in part, by the minimum dimension of the particulate, in this case the thickness of the flattened cryomilled particles. Since we idealize the particles as continuously flattened during cryomilling, the relative thickness scales approximately with the surface area. Thus, regardless of the kinetic pathway, to first order the rate of hydrogen uptake should scale with the specific surface area, which is plotted in Figure 8. While there is a general trend of shorter uptake times for greater surface area, the samples cryomilled for 1 and 2 hours are not self-consistent in this regard. There is no clear explanation for this apparent inconsistency; morphologically (Figure 1)

the powders cryomilled for 1 and 2 hours respectively are very similar except that longer cryomilling time results in thinner disks of larger diameter. However, there are likely competing factors in the process of uptake, such as the role of microstructural defects on the diffusive transport of hydrogen in the bulk. Hydrogen trapping, for example, impedes bulk diffusion, thus high density of hydrogen traps (such as dislocations or grain boundaries) can, in principle, reduce the apparent diffusivity and limit rates of uptake. Longer cryomilling times or higher-energy milling conditions (e.g., more milling media) could conceivably result in microstructures that promote diffusion-limited processes that reduce the rate of hydrogen uptake. More work is necessary to clarify the kinetic pathways as well as establish relationships between the processing conditions and the rates of hydrogen uptake in the Pd-10Rh alloy.

4 Conclusions

In the present study, Pd-10Rh powder was cryomilled for times of 1, 2 and 8 hours to refine the grain size and increase dislocation density. The pressure-composition isotherms for sorption of hydrogen were measured for the resulting powder and related to the observed morphological and microstructural differences. The morphology and microstructure of the Pd-10Rh particles evolved in several ways during the cryomilling process:

- the particles are flattened during cryomilling without significant particle fracture becoming thin disks compared to the initially spherical (atomized) particles;
- the specific surface area of the powder increased by an order of magnitude after 8 hours of cryomilling compared to the atomized, spherical particulate;
- the dislocation density increased by more than an order of magnitude to values greater than 10^{15} m^{-2} ;

- XRD line broadening reveals that the crystallite size decreased to <100 nm after 8 hours of cryomilling, compared to ~230 nm in the atomized powder.

This particle and microstructural evolution leads to changes in hydrogen sorption characteristics, in particular:

- the maximum hydrogen concentration in α -hydride phase ($\alpha_{\max}$) increases with longer cryomilling time;
- longer cryomilling time also results in a flatter pressure plateau (for the $\alpha \rightarrow \beta$ phase transition) and greater equilibrium hydrogen concentration (at fixed pressure);
- cryomilling dramatically improves the rate of hydrogen uptake compared to the atomized powder.

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Tables

Table 1. Powder and microstructural characteristics of atomized and cryomilled Pd-10Rh powders (1h, 2h and 8h refer to cryomilling times in hours). Crystallite size and microlattice strain determined from X-ray diffraction line profile analysis.

Powder	Surface area (m ² /g)	Crystallite size (nm)	Microlattice strain	Dislocation density (m ⁻²)
atomized	0.037	230	0.002	1.2 x 10 ¹⁴
1h	0.088	270	0.012	5.6 x 10 ¹⁴
2h	0.13	130	0.010	1.0 x 10 ¹⁵
8h	0.44	77	0.014	2.4 x 10 ¹⁵

Table 2. Hydrogen uptake and solubility characteristics of atomized and cryomilled Pd-10Rh powders (1h, 2h and 8h refer to cryomilling times in hours)

Powder	$\theta_{\max}$ (H/M)	$\alpha_{\max}$ (H/M)	c_H [P=80 kPa] (H/M)	c_H [P=101 kPa] (H/M)	Absorption half-life (sec)
atomized	0.0050	0.046	0.54	0.66	88
1h	0.0093	0.050	0.60	0.69	28
2h	0.011	0.057	0.62	0.71	42
8h	0.014	0.070	0.65	0.72	8

Figure captions

Figure 1. SEM micrographs of (a) atomized Pd-10Rh, and Pd-10Rh particles cryomilled for (b) 1h, (c) 2h, and (d) 8h; and SEM micrographs of cross-sections of (e) atomized Pd-10Rh, and Pd-10Rh particles cryomilled for (f) 1h, (g) 2h, and (h) 8h.

Figure 2. X-ray diffraction patterns of atomized and cryomilled Pd-10Rh.

Figure 3. TEM micrographs of (a) atomized Pd-10Rh particles, and Pd-10Rh particles that were cryomilled for (b) 1 hour, (c) 2 hours, and (d) 8 hours.

Figure 4. PC isothermal absorption/desorption curves for atomized and cryomilled Pd-10Rh. Inset: PC isothermal absorption at low H/M concentrations. The reader is referred to the text of the manuscript for the definitions of $\theta_{\max}$ and $\alpha_{\max}$.

Figure 5. Hydrogen concentration parameters ($\theta_{\max}$ and $\alpha_{\max}$) as a function of measured surface area.

Figure 6. Hydrogen concentration parameters as a function of (a) dislocation density and (b) subgrain boundary volume estimated as the inverse crystallite size ($1/D$).

Figure 7. Hydrogen uptake in Pd-10Rh as a function of time for atomized powder and after cryomilling for times of 1, 2 and 8 hours.

Figure 8. Half-life for hydrogen uptake in Pd-10Rh as a function of specific surface area. The dotted line is an arbitrary trend line.

Figure 1. parts a-b

Figure 1. parts c-d

Figure 1. parts e-f

Figure 1. SEM micrographs of (a) atomized Pd-10Rh, and Pd-10%Rh particles cryomilled for (b) 1h, (c) 2h, and (d) 8h; and SEM micrographs of cross-sections of (e) atomized Pd-10Rh, and Pd-10%Rh particles cryomilled for (f) 1h, (g) 2h, and (h) 8h.

Figure 2. X-ray diffraction patterns of atomized and cryomilled Pd-10Rh.

Figure 3. parts a-b

Figure 3. TEM micrographs of (a) atomized Pd-10Rh particles, and Pd-10Rh particles that were cryomilled for (b) 1 hour, (c) 2 hours, and (d) 8 hours.

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(a)

(b)

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