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Dihydride formation in the palladium-rhodium alloys under high hydrogen pressure



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ABSTRACT

Palladium, rhodium and their alloys were studied in a diamond anvil cell in a high pressure hydrogen atmosphere up to 20 GPa by X-ray diffraction at room temperature. Formation of a monohydride with H/(Rh + Pd) = 1 ratio was observed for each alloy at hydrogen pressures less than 3 GPa. The corresponding volume expansion of the metal lattice was 2.2 –2.8 Å³ per metal atom. A formation of the dihydride with H/(Rh + Pd) = 2 was observed at a hydrogen pressure around 10 GPa for the alloys with rhodium content Rh/ (Rh + Pd) \geq 50 at.%. The dihydride formation is accompanied by a volume expansion of metal lattice by 3.2–3.9 Å³ per metal atom. For Pd-rich alloys with Rh/(Rh + Pd) \leq 25 at.% and pure Pd the dihydride formation was not observed up to maximum reached hydrogen pressure. All observed phases had a fcc structure of metal lattice.

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Introduction

Metal hydrides are important hydrogen and energy storage materials. Most transition metals form hydrides at sufficiently high pressures of hydrogen [1]. Among the group VI–XII transition metals no hydrides were known until recently with hydrogen-to-metal ratio greater than one. With the recent development of the diamond anvil cell technique three new polyhydrides were found at hydrogen pressures higher than 10 GPa: RhH₂ [2], IrH₃ [3] and FeH₃ [4]. Since then a possibility for the formation of other new transition metal polyhydrides has drawn attention.

New hydrides may have attractive properties such as superconductivity. According to the rigid band model, which treats hydrogen as an electronic donor to a weakly deforming conduction band of the host metal, as proposed by Ponyatovskii [5], rhodium dihydride should have an electronic structure similar to palladium monohydride, which is a superconductor with $T_c = 9$ K [6]. Due to high frequency optical phonons of hydrogen vibrations, as high T_c as 200 K could occur in hydrides, as recently found in the sulfur-hydrogen system at P = 150 GPa [7]. It was later suggested [8] that H_2S solid most likely decomposes under pressure via the route $3H_2S \rightarrow 2H_3S + S$, and it is the H_3S phase which possess high temperature superconductivity.

The Pd-H₂ system is historically the first metal-hydrogen system that attracted research activities. The superconducting transition temperature of palladium hydride rises dramatically with the increase of its hydrogen content, so it would be interesting to synthesize over-stoichiometric palladium hydride to study its superconducting properties. Despite earlier reports [9], no one succeeded in doing that.

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To facilitate this task, we alloyed palladium with rhodium, which is the nearest neighbor of palladium in the periodic table.

In the present study rhodium, palladium and their alloys were investigated under hydrogen pressure up to 20 GPa. Our aims were to verify the possibility of a dihydride formation in such alloys and to determine the corresponding formation pressures as a function of alloy composition.

Both rhodium and palladium have a fcc metal lattice. They form continuous substitutional solid solutions. The monohydrides are formed, when hydrogen atoms fill octahedral interstitial positions, forming a NaCl-type structure [10,11]. In the dihydrides tetrahedral interstitial positions are filled instead, forming a CaF_2 -type structure.

A monohydride formation in the Pd–Rh alloys was studied in Ref. [12]. At room temperature an equilibrium $Rh + \frac{1}{2}H_2 =$ RhH takes place at a hydrogen pressure between 2.5 and 3.8 GPa [13]; palladium forms substoichiometric hydride PdH_{0.63} at P ~ 700 Pa, and the H/Pd content of the hydride continuously increases with pressure, reaching 1 at P ~ 1 GPa [14].

Experimental details

We used a diamond anvil cell (DAC) of the modified brilliant type with a culet diameter of ~400 μ m. A 200 μ m hole was spark-drilled in a rhenium gasket preindented to ~50 μ m thickness. Sample foils were 5–10 μ m thick and had compositions Pd, Pd₇₅Rh₂₅, Pd₅₀Rh₅₀, Pd₂₀Rh₈₀ and Rh. The compositions were independently controlled based on the intensity ratio between the X-ray fluorescence lines of Rh and Pd. The pressure was measured by a ruby fluorescence method [15], using an excitation from a 633 nm HeNe laser and a THR1000 spectrometer for spectra recording. Hydrogen loading technique is described elsewhere [16]. Hydrogen was always in excess, serving both as a reagent and a pressure transmitting medium.

After initial clamping of hydrogen in a DAC at a pressure of about 0.3 GPa the compression force was increased in steps by a lever mechanism. Each step resulted in a pressure drift due to gasket relaxation and hydrogen consumption by the sample and the gasket. This drift slowed down with time. The pressure was measured before and after each X-ray diffraction measurement was done, and the difference between these values was typically about 1 GPa at pressures about 10 GPa and higher. The pressures referred further are the pressures after the X-ray measurements.

X-ray powder diffraction was measured by the energydispersive method with a polychromatic radiation from a conventional tungsten target tube [17] collimated down to about 100 μ m to avoid diffraction from the gasket material. The scattering angle 2 θ was fixed during each compression-decompression cycle, and it was calibrated for each cycle independently based on the diffraction patterns of the hydrogen-free initial alloys and assuming Vegard law. The typical 2 θ value was about 20°, corresponding to E*d ~35 keV*Å. The energy scale was calibrated for each spectrum independently using the positions of the K α and K β X-ray fluorescence lines of Pd and Rh as a standard and assuming linear dependence between the channel number of the multichannel analyzer and the photon energy. Accumulation time was different for each pattern, typically in the range from $5*10^3$ to 10^5 s. All experiments were conducted at room temperature.

Results and discussion

All observed phases had an unordered fcc lattice of metal atoms, as monitored by X-ray diffraction. Few diffractograms showed two-phase mixtures, and the rest had shown single phases. The two phase states of the samples were observed when a formation of a higher hydride had started. In all cases, after pressure increase the diffraction peaks from the lower hydride disappeared. No hydrogen-induced decomposition into rhodium-rich and palladium-rich phases was observed for any alloy. Typical X-ray diffraction patterns of the Pd₂₀Rh₈₀ alloy measured at different hydrogen pressures are shown in Fig. 1.

The K β fluorescence lines on every pattern had shoulders towards higher energies. Their presence did not depend on the value of 2 θ , indicating that these shoulders were the characteristic features of the K β absorption edges, and were not of diffraction origin. Same features were observed in our previous experiments [18,19].

The lattice parameter was calculated for each alloy as a function of hydrogen pressure using the positions of the (111) and (200) peaks in the diffraction patterns. If the position of one of these peaks could not be determined reliably, e.g. due to overlapping with X-ray fluorescent lines or due to insufficient



Fig. 1 – Typical energy-dispersive X-ray powder diffraction patterns of a Pd₂₀Rh₈₀ sample in a DAC measured during hydrogen pressure increase. The patterns consist of the Xray fluorescent lines from the sample in the range of 20–24 keV (marked as Rh/Pd K α/β), the diffraction peaks from a rhenium gasket ("Re gasket"), the diffraction peaks from the sample ("Me", "MeH" and "MeH₂") and the detector artefacts at E < 14 keV. The cathode voltage was –40 kV, the anode current was 20 mA, and the scattering angle 20 corresponded to E*d = 37.7 keV*Å. All patterns had different accumulation times, typically from 5*10³ to 10⁵ s.



Fig. 2 – a–e. Hydrogen pressure dependencies of the lattice volume per metal atom for each studied alloy. The symbols present the experimental X-ray diffraction data, and the lines are guides for an eye. The data on pure palladium compressibility [20] are shown by the dashed line in Fig. 2a. In Fig. 2b the volume discontinuity at 1.6 GPa results from a monohydride formation, and an anomaly at 17 GPa is a supercritical anomaly, discussed in the text. The first and the second volume discontinuities in Fig. 2c–e correspond to a mono- and a dihydride formation respectively. The data on pure rhodium compressibility [21] are shown by the dashed line in Fig. 2e.

counting statistics, the lattice parameter was calculated using the other peak. The resulting lattice volumes are presented in Fig. 2a-e separately for each alloy.

No dihydride formation was observed up to the hydrogen pressures of 23 GPa and 20 GPa for pure palladium and the Pd₇₅Rh₂₅ alloy respectively. The rest of the alloys formed dihydrides in the pressure range of 10-12 GPa. Hydrogen content estimation and justification of the term "dihydrides" will be given further in the text.

The compressibility of palladium hydride is similar to the compressibility of pure palladium, as shown by the solid and the dashed lines respectively in Fig. 2a. This behavior is typical for the stoichiometric transition metal hydrides [22]. Rhodium is less compressible than its hydrides, as shown by the dashed and the solid lines in Fig. 2e. The bulk modulus of rhodium $B_{Rh} \approx 300$ GPa (a fit of the results of Ref. [21]) is considerably higher than that of palladium $B_{Pd} \approx 200$ GPa (a fit of the results of Ref. [20]), thus, the bulk modulus is strongly affected by a number of electrons in the conduction band. Additional electrons brought into the conduction band of rhodium by hydrogen lead to the decrease in bulk modulus. Firstprinciples calculations give the following values of the bulk moduli: $B_{Rh} = 250$ GPa, $B_{RhH} = 232$ GPa, $B_{RhH2} = 190$ GPa [23], $B_{Pd} = 166 \text{ GPa and } B_{PdH} = 177 \text{ GPa}$ [24].

Regretfully, a narrow stability range of rhodium monohydride along with an uncertainty of volume determination prevents us from quantitatively compare the compressibilities of two rhodium hydrides.

Only limited data are available on a direct determination of the hydrogen content of hydrides formed under high pressure. However, the hydrogen content can be estimated indirectly from the volume expansion of the metal lattice during the hydrogen absorption step. Hydrogen occupies octahedral interstitials in many transition metals, resulting in an expansion of a metal lattice typically by 2.0–2.5 Å³ per H atom [22]. For rhodium and palladium monohydrides the corresponding volume expansions are close to each other, being 2.41 Å³ per H atom [25] and 2.52 Å³ per H atom [26] respectively. Hydrogeninduced volume expansion in the monohydrides of the Rh-Pd alloys virtually does not depend on alloy composition, thus it can serve as a reliable means for the hydrogen content estimation [12].

The volume expansion for the transition metal dihydrides where hydrogen occupies tetrahedral interstitial positions in a close-packed metal lattice can vary from 2.2 Å³ (for TiH₂) to 2.9 Å³ (for NbH₂) per H atom. For the rare-earth metal dihydrides with a CaF2-type structure the volume expansion varies dramatically from 1.1 Å³ (for YH₂ [27]) to 3.8 Å³ (for LaH₂ [28]) per H atom.

The composition of rhodium dihydride H/Rh = 2 was determined on the basis of the lattice volume difference between RhH₂ and Rh, which was estimated to be 3.2 Å³ per H atom [2]. It is reasonable to assume that hydrogen occupies tetrahedral interstitial sites in the dihydides of the Rh-Pd alloys in the same way as in RhH₂. By analogue to the monohydrides of the Rh-Pd alloys one would expect that the volume expansion caused by hydrogen occupation of tetrahedral interstitials is independent from alloy composition.

Our measurements corroborate the results of Ref. [2] for rhodium in a hydrogen atmosphere. The observed

1 V(MeH)-V(Me) 30 10 20 40 50 60 70 80 90 Pd at.% Fig. 3 - Volume expansions of the Rh-Pd alloys at the first

and the second hydrogen absorption steps.

discontinuities of the metal lattice volumes at the phase transformations are plotted together in Fig. 3. We estimate that the difference in the lattice volumes of RhH₂ and Rh is 6.5(10) $Å^3$ per metal atom, or 3.2(5) $Å^3$ per H atom. The first value is the sum of the volume differences "V(MeH₂)-V(MeH)" and "V(MeH)-V(Me)", shown by the black and the gray symbols respectively in Fig. 3. Similarly, for the Pd₂₀Rh₈₀ and Pd₅₀Rh₅₀ alloys the differences between the lattice volumes of the dihydrides and the initial alloys, calculated per metal atom, are 5.8(10) $Å^3$ and 6.0(10) $Å^3$ respectively.

Within the volume determination uncertainty we do not observe a significant departure of these values from that for the difference in the lattice volumes of RhH₂ and Rh. Would the hydrogen content of these compounds deviate from H/ (Rh + Pd) = 2, there should be such a departure. We conclude that the hydrogen content of these compounds is close to that of RhH₂, justifying the use of term "dihydride" for them.

The pressures of phase transformations against the Rh/ (Rh + Pd) content are presented by the symbols in the phase diagram shown in Fig. 4. The solid symbols other than the circle show pressures at which the formations of the higher hydrides were first observed, and the empty ones present pressures at which the decompositions of the higher hydrides were first observed. The corresponding pressures are further referred to as the formation and decomposition pressures respectively. The equilibrium pressures must lay between these two sets of symbols. It is widely accepted that the equilibrium conditions for the metal hydride formation reactions are closer to the decomposition conditions rather than to the midpoint between decomposition and formation [29,30]. Assuming decomposition pressures as the equilibrium ones allows us to estimate standard thermodynamic properties of the considered compounds and to compare them with the results of ab-initio calculations [2]. In our experiments the decomposition pressures were reliably determined only for the Rh–H system; they are $P_1^{eq} = 2.1$ GPa and $P_2^{eq} = 4.5$ GPa for RhH and RhH₂ respectively.

The standard Gibbs free energies for the reactions Rh + 1/2 $2H_2 \ \rightarrow \ RhH$ and $RhH + 1/2H_2 \ \rightarrow \ RhH_2$ at $P_0 = 1$ bar and T = 298 K were estimated as following:





Fig. 4 - Tentative phase diagram of the Pd-Rh system under high hydrogen pressure at room temperature. The symbols other than the circle show pressures at which a formation and decomposition of mono- and dihydrides were observed experimentally. The squares present data on the Rh-H system from Ref. [2], the diamonds present data on the monohydride formation and decomposition from Ref. [12], and the triangles are present data. The blue and the red lines represent tentative equilibrium pressures for the Me $+ \frac{1}{2}H_2 =$ MeH and MeH $+ \frac{1}{2}H_2 =$ MeH₂ reactions respectively. The cyan, white and magenta areas are the stability fields of primary hydrogen solution in alloys, monohydride and dihydride respectively. The critical point where the monohydride ↔ dihydride equilibrium line terminates is shown by a red circle. The supercritical region is colored by a gradient filling. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\begin{split} &\Delta G^0 \bigg(Rh + \frac{1}{2} H_2 \rightarrow RhH \bigg) = \int\limits_{P_1^{eq}}^{P_0} \Delta V dP = \int\limits_{P_1^{eq}}^{P_0} \bigg(V_{RhH} - V_{Rh} - \frac{1}{2} V_{H_2} \bigg) dP \approx \\ &\approx - (V_{RhH} - V_{Rh}) P_1^{eq} + \frac{1}{2} \int\limits_{P_0}^{P_1^{eq}} V_{H_2} dP \approx + 22(2) \ kJ/mol, \end{split}$$

$$\begin{split} &\Delta G^0 \left(RhH + \frac{1}{2} H_2 \rightarrow RhH_2 \right) = \int\limits_{P_2^{eq}}^{P_0} \Delta V dP = \int\limits_{P_2^{eq}}^{P_0} \left(V_{RhH_2} - V_{RhH} - \frac{1}{2} V_{H_2} \right) dP \approx \\ &\approx - \left(V_{RhH_2} - V_{RhH} \right) P_2^{eq} + \frac{1}{2} \int\limits_{P_0}^{P_2^{eq}} V_{H_2} dP \approx + 27(2) kJ/mol, \end{split}$$

where $V_{RhH} - V_{Rh} = 2.6 \text{ Å}^3/(\text{Rh} \text{ atom})$ and $V_{RhH_2} - V_{RhH} = 3.9 \text{ Å}^3/(\text{Rh} \text{ atom})$ are the volume differences shown in Fig. 3, and the hydrogen molar volume V_{H_2} was calculated using the equation of state from Ref. [31]. The literature value for the first reaction $\Delta G^0 \approx +24 \text{ kJ/mol H}$ [13] reasonably agrees with present estimate.

One should refer these values to 0 K to make a comparison with the results of the ab-initio calculations in Ref. [2]. The difference in the standard Gibbs free energies at 298 K and 0 K for hydrogen can be taken from Ref. [32]: $G_{H_2}^0(298K) - G_{H_2}^0(0K) = H_{H_2}^0(298K) - H_{H_2}^0(0K) - TS_{H_2}^0(298K) = -30.5 \ kJ/mol H_2$. The difference in the thermodynamic properties of Rh and its hydrides mostly comes from the phonon contribution, which can be estimated if the vibrational frequency ω of hydrogen atoms in the metal lattice is known [30]. For example, $G_{RhH}^0(298K) - G_{RhH}^0(0K) - G_{Rh}^0(298K) + G_{Rh}^0(0K) = 3RT \ln(1 - \exp(-\hbar\omega/kT)) = -370 \ J/mol \ H$, where $\hbar\omega = 78 \ meV$ in RhH, as measured by inelastic neutron scattering in Ref. [25]. We neglect this contribution, because it is smaller than the uncertainty in ΔG^0 .

At $P_0 = 1$ bar and 0 K we obtain $\Delta G^0 \left(Rh + \frac{1}{2}H_2 \rightarrow RhH \right) =$ +7(2) kJ/mol H and $\Delta G^0 \left(RhH + \frac{1}{2}H_2 \xrightarrow{\sim} RhH_2 \right) = +12(2)$ kJ/mol~H. In Ref. [2] the enthalpies for the reactions Rh + $1/2H_2 \rightarrow$ RhH and Rh + H₂ \rightarrow RhH₂ were calculated ab initio at T = 0 K as a function of pressure, particularly, at ambient pressure $\Delta H^0_{calc}\left(Rh + \frac{1}{2}H_2 \rightarrow RhH\right) \approx +0.12 \text{ eV}/f.u. \text{ and } \Delta H^0_{calc}\left(Rh + H_2 \rightarrow H_2 \rightarrow H_2 + H_2 + H_2 \rightarrow H_2 \rightarrow H_2 + H_2 \rightarrow H_2 \rightarrow H_2 \rightarrow H_2 + H_2 \rightarrow H_$ RhH_2 $\approx +0.07 \ eV/f.u.$, which corresponds to ΔG_{calc}^0 $\left(\mathrm{Rh}+\frac{1}{2}\mathrm{H}_{2}\rightarrow\mathrm{RhH}\right)\approx+11\ kJ/mol\ \mathrm{H}$ and $\Delta G_{calc}^{0}\left(\mathrm{RhH}+\frac{1}{2}\mathrm{H}_{2}\right)$ \rightarrow RhH₂ ≈ -5 kJ/mol H. One can see that the accuracy of the calculations is not good enough to predict higher ΔG_{calc}^0 for the $RhH+1/2H_2 \rightarrow RhH_2$ reaction than for $Rh+1/2H_2 \rightarrow RhH.$ Moreover, the $\Delta G_{calc}^0 \left(RhH + \frac{1}{2}H_2 \rightarrow RhH_2 \right)$ has a wrong sign. We think that there can be a systematical problem in the ab-initio calculations, which leads to the underestimation of the Gibbs free energies for hydrogen-rich phases, and, correspondingly, to the underestimation of their formation pressures.

The behavior of rhodium under hydrogen pressure differs dramatically from that of cobalt and iridium, which are in the same group in the periodic table. The hydride formation in the Co–H system is accompanied by a phase transition from hydrogen solid solution in a hcp metal lattice to a monohydride with a NaCl-type structure at P = 4.5 GPa with no further hydrogen absorption up to 22 GPa [33]. The hydride formation in the Ir–H system is accompanied by a phase transition from a fcc to an unusual distorted simple cubic structure of metal lattice at P = 55 GPa, and the hydride has a tentative composition H/Ir = 3 [3].

Absence of the dihydride formation of pure Pd and $Pd_{75}Rh_{25}$ would suggest either that the dihydride formation pressure drastically increases for alloys with composition Rh/(Rh + Pd) less than 50%, or that the dihydrides are not formed at all for these alloys. We think that the second possibility is realized in analogue to the systems Pd–Ag–H, Pd–Au–H and Pd–Pt–H (see Ref. [12] and references therein). In these

systems the discontinuity in the hydrogen solubility at room temperature is observed only for certain compositions, e.g. for palladium content more than 80 at.%. For palladium content below a certain critical value, the hydrogen solubility changes continuously with hydrogen pressure.

The point where the phase transition line terminates is called a critical point. Such critical points are frequently found at the pressure-temperature phase diagrams of binary metalhydrogen systems.

In our case sharp phase transformations, corresponding to the dihydride formation are observed only for rhodium rich alloys. There should be a limiting alloy composition such that alloys with compositions between this critical composition and pure palladium do not demonstrate sharp phase transition. We estimate this critical rhodium content as Rh/ (Rh + Pd) = 38(12) at.% because it should be located between 25 and 50 at.% Rh.

It is known that the baric hysteresis between the formation and decomposition pressures decreases to zero when the composition approaches a critical value. In our case a critical pressure can be estimated to be 11.5(10) GPa by extrapolating the dihydride formation pressure to the critical composition. The resulting location of the critical point at the Pressure vs. Rh/(Rh + Pd) phase diagram is shown by a circle in Fig. 4. The equilibrium curve for the dihydride formation connects the critical point with the equilibrium point for the reaction RhH $+\frac{1}{2}H_2 = RhH_2$, which takes place at $P_{\rm H_2} = 4.5$ GPa.

A region at the phase diagram where the continuation of the phase transition line beyond the critical point falls into is called a supercritical region. This region is shown in Fig. 4 by a gradient filling. In a supercritical region no sharp phase transition is observed, however, a fraction of hydrogen atoms occupy tetrahedral interstitials, causing continuous lattice expansion.

The volume increase for the $Pd_{75}Rh_{25}$ alloy in the pressure range between 13.5 and 17 GPa in Fig. 2b can be naturally interpreted as a supercritical anomaly. Would there be no critical point nearby, this anomaly should not be expected.

Unfortunately, our data are not good enough to estimate a critical hydrogen composition. We do not observe a significant departure of the "V(MeH₂)–V(MeH)" volume differences in Fig. 3 from a constant value for alloys with Rh/(Rh + Pd) \geq 0.5, despite this difference should decrease to zero for the alloy with critical rhodium content. Further studies are needed to clarify the behavior of the "V(MeH₂)–V(MeH)" volume differences in the immediate vicinity of the critical point.

Conclusions

After the recent discovery of rhodium dihydride, considerable evidence was found that some other transition metals in groups VI–XII can also form polyhydrides at high hydrogen pressure.

An alloying of rhodium with palladium up to 50 at.% increases the dihydride formation pressure, and at higher palladium concentration the dihydride does not form. No excess of hydrogen solubility in palladium over H/Pd = 1 was observed under hydrogen pressures up to 23 GPa.

The estimated values of the standard Gibbs free energies for the formation reactions of rhodium mono- and dihydride provide basis for the refinement of the ab initio calculation methods.

The work is in progress to study the superconducting properties of the produced dihydrides.

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